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PREFACE

The study of electrochemical reactions, which are necessarily heterogeneous, requires as one of its bases a knowledge of the factors determining the adsorption equilibrium between reacting ions or molecules at the electrode and in solution. For a small number of simple ions (principally cations) this equilibrium is determined almost entirely by classical electrostatic interactions between the ions and the field of the electrode; in other cases, effects of a more specifically "chemical" nature are apparent. The adsorption of simple ions at electrodes has been the focus of studies of a number of previous workers over the last 50 years or more, the principal contributions being those of Gouy, Helmholtz, Stern, Chapman, Frumkin and more recently of the late Dr. Grahame.

The corresponding problem of the adsorption of organic ions and molecules at electrodes and the related problem of the structure of the double layer in such systems has been relatively less developed despite the interesting effects such additives have on various electrode reactions - effects which find practical application in the fields of corrosion inhibition and electrodeposition of metals.

The objects of the work described in this thesis

have hence been to examine by experiment and theory the electrochemical adsorption of a selection of N-heterocyclic and aromatic organic bases, their conjugate ions and their quaternary salts at solid and liquid (mercury) electrodes. The experimental investigations of adsorption at mercury have been made by electrocapillary measurements and at solid electrodes viz. nickel, silver and copper, by means of a novel technique developed conjointly by the author and another co-worker.

The choice of such studies was guided by three major considerations: (1) the lack of a full understanding of the structure of the electrical double layer at metal-solution interfaces, particularly with solutions of neutral and ionic organic solutes; (2) the necessity for clarification of the role of adsorption in certain electrode processes in which such compounds are involved; this is an important requirement since the interpretation of electrode processes is dependant on an exact knowledge of surface concentrations of reactants and the distribution of potential in the double layer; and (3) the absence in the literature of a thermodynamically unambiguous method for determining the reversible adsorption of organic molecules and ions at solid electrodes.

In the work to be described, emphasis will be placed on physicochemical aspects of the behaviour of the adsorbates rather than on the general chemistry of the organic compounds

per se. The desired aim therefore has been to present in the Introduction (and Appendix) a unifying account of those basic principles and problems which are common to Electrochemistry and Chemisorption. Although well established conclusions in these two individual fields have been adequately recorded in the literature, only a small degree of successful correlation between them has been achieved.

A detailed knowledge of recent advances in the above-mentioned subjects is not presupposed; only a general acquaintance with fundamental ideas is assumed. The essential background will thus be contained in a review presented in two parts: (1) an Introduction and (2) for convenience, an Appendix covering matters in the field of chemisorption which are of indirect, but nevertheless fundamental, interest to electrochemists. The relevant literature has been reviewed in a comprehensive manner with a conscious effort to avoid excessive prejudice and parochialism. This literature survey was also undertaken with the intention of subsequent publication in more condensed form as a critical review.

The work on solid electrodes has been reported in two papers: (1) B.E. Conway, R.G. Barradas and T. Zawidzki, *J. Phys. Chem.*, 62, 676 (1958); (2) B.E. Conway and R.G. Barradas, *Trans. Phila. Symposium on Electrode Processes 1959*, The Electrochemical Society, John Wiley, New York, (in press).

Part of the work on the electrochemical adsorption of organic bases and their conjugate acids, in the form of two full papers, has been accepted for publication by the journal "Electrochimica Acta" and is at present in press. The papers are entitled:

Electrochemical Adsorption of Organic Bases and their Conjugate Acids, Part I: Adsorption of Neutral Bases at Mercury;

Part II: Comparison of the Adsorption of the Bases and their ions at Mercury.

The sections of the thesis on the ionic components of charge in the electrical double layer, and that connected with the Zin and Markov effect will be published elsewhere in the near future.

The studies of adsorption on mercury will be presented in three chapters as Part I of the thesis. Chapter II contains the experimental details of this work, Chapter III the results and the ensuing discussion including derived data will be treated in Chapter IV. This division is necessitated by considerations of length and convenience. In order to conform with University regulations, the work on solid electrodes, embodied in Chapter V, will be presented as Part II of the thesis. No attempt has been made to incorporate the experimental section of this work into Chapter II since such a discussion will tend to create discontinuity and inconvenience to the reader.

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To some the transition from analytical and forensic chemistry (the writer's previous field of experience) to an academic world of electrochemistry may not represent too great a step, but to one of limited aptitude and versatility, the stride may appear to be gigantic. It is in this respect that the writer wishes to record very profound appreciation to his research supervisor, Dr. B.E. Conway. The writer's incursion into "materia electrochemica" is entirely due to Dr. Conway, who generously proffered not only constant scientific training and guidance, but also considerable personal interest. It is sincerely hoped that whatever success may accompany this thesis will reflect credit to his able and patient research direction.

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ABSTRACT

Electrocapillary measurements are reported for the adsorption of a series of heterocyclic and aromatic bases, and their conjugate ions, at the mercury electrode. The adsorption isotherms are derived for various electrode potentials, and standard electrochemical free energies $\Delta \bar{G}^0$ of adsorption are deduced and related to molecular and electronic structure of the adsorbates.

Specific π -orbital interaction effects are indicated which determine the orientation of the bases at the electrode. It is shown that dipole interaction effects should lead to variations of $\Delta \bar{G}^0$ with the $3/2$ power of surface coverage θ ; this prediction is confirmed experimentally. The variation of $\Delta \bar{G}^0$ with $\theta^{3/2}$ has two distinct linear regions, the change of slope $(\partial \Delta \bar{G}^0 / \partial \theta^{3/2})_{\theta}$ being related to molecular orientation at high fields and coverages. The effects are closely related to the shifts of the potential of the electrocapillary maximum (e.c.m.) observed in the solutions of the bases. The observed $\Delta \bar{G}^0$ values at the e.c.m. are related to those found for the adsorption of two bases at the air/water interface.

For the ions, hydration effects are calculated and the role of π -orbital interactions with the electron-deficient metal surface on the positive branch of the electrocapillary curve is discussed. Energies of π -orbital

interaction of hydrocarbons with the mercury electrode are estimated from previous work and compared with the free energies of adsorption calculated for the organic ions. Ionic interaction effects in the surface layer are investigated by evaluating $\Delta \bar{G}^\circ$ as a function of ϕ . Deviations from an expected linear relationship between $\Delta \bar{G}^\circ$ and $\phi^{1/2}$ are found, and are consistent with Van der Waals attractive forces treated by other authors. Changes of the potential of the electrocapillary maximum have been evaluated and appear to be related to the degree of interaction of the ions of the bases with the mercury surface through π -orbital bonding in a way similar to that for the adsorption of the corresponding unionized bases.

The ionic components of charge within the electrical double layer as a function of potential have been studied. Electrocapillary curves for various concentrations of pyridine, methylpyridinium chloride and quinoline, in several solutions with variable concentrations of potassium chloride and hydrochloric acid, respectively, were obtained. From these data, calculations were made of the charge on the solution side of the metal-solution interface (q_s), and of the surface excesses of positive ions ($\Gamma_{H_3O^+}$, Γ_{K^+} , and Γ_{base^+}), negative ions (Γ_{Cl^-}) and neutral molecules (Γ_{base}). These quantities lead to a detailed picture of the structure and

charge distribution in the double layer in the presence of the organic bases and their ions.

An experimental study of the Eain and Markov Effect was made for the specifically adsorbed organic cations. In all cases examined, the plot of the potential of the electrocapillary maximum E_{max}^0 (with respect to the potential of a calomel electrode) was a linear function of the logarithm of the concentration of the organic cation, and the slope was found to be less than $\frac{kT}{e}$, which is in agreement with Stern's theory of the electrical double layer. The thermodynamic relationship

$$\left(\frac{\partial E_{\text{max}}^0}{\partial \ln a_+} \right)_{q_M} = - \frac{kT}{e} \left(\frac{\partial q_+}{\partial q_M} \right)_{a_+}$$

has been deduced and is quantitatively consistent with the experimental results.

In the absence of any theory of "the Eain and Markov Effect for neutral molecules" an analysis, similar to that for ions, was made for the un-ionised organic bases. The following relationship was derived thermodynamically:

$$\left(\frac{\partial E}{\partial \ln a_A} \right)_{q_M} = - RT \left(\frac{\partial \Gamma_A}{\partial q_M} \right)_{a_A}$$

and it was observed experimentally that this relationship gave only a fair but not exact representation of the shift in the potential of the e.c.m. with changes in the logarithm of the

activity of the neutral organic substrate. Plots of $E^{0.0.2.0.}$ versus $RT \ln C_A$ gave slopes which agreed only in order of magnitude with those slopes of the plots of Γ_A against q_H (at constant a_A).

Finally, a spectrophotometric method was developed for the direct determination of the adsorption of conjugated heterocyclic and aromatic molecules, their ions, and their quaternary salts, at solid electrodes. The effects of charge and ring size of the organic additives, the role of varying solvents and acids, the comparison of strength of adsorption of some adsorbates at copper, nickel and silver, the effect of polarization applied to the electrodes and the evaluation of thermodynamic parameters of adsorption were investigated. In a number of cases, the results could be related to those obtained at mercury from the electrocapillary studies.

CHAPTER I

INTRODUCTION

A. PRELIMINARY COMMENTS

In this Introductory Chapter to the thesis, the aim has been to bring together in the form of a comprehensive and critical review some of the main theories of electrochemical adsorption and of the structure of the double layer at electrodes together with an examination of the thermodynamic theory of electrocapillarity which is used extensively in the interpretation of the experimental results obtained in the present work. Since interest in adsorption at electrodes is closely connected with the interpretation of the kinetics of electrode processes, these matters have also been discussed in this Chapter.

(1) Definitions

It is appropriate to begin with the clarification of a few fundamental concepts which will be used repeatedly in the subsequent text.

Matter at the boundary of two phases possesses certain properties which differentiate it from matter uniformly distributed in either of the continuous phases separated by the interface. The tendency for accumulation of a component in one or more of the phases to occur at a surface is known as ADSORPTION. The contact of "immiscible" phases may, in addition to adsorption, result in limited penetration of one phase by the

other, and this is known as ADSORPTION.

The phenomenon of adsorption arises from the fact that atoms in any surface are subject to unbalanced forces of attraction perpendicular to the surface plane and therefore possess a certain "unsaturation". It is this unsaturation which explains why perfectly clean metallic surfaces are relatively highly energetic and the mere touching of two such surfaces would be sufficient to produce a weld. The main work of "saturating" the surface forces is usually accomplished by the condensation of a single layer of molecules and in such a case the adsorption is termed UNIMOLECULAR and the film a MONOLAYER. Adsorption takes place not only with a decrease in surface (free) energy but also often with a decrease in entropy because, by confining an adsorbed molecule to a thin surface layer, at least one translational and often one or more rotational degrees of freedom are lost. This is accompanied usually by a corresponding decrease in the heat content of the adsorbate; hence adsorption is nearly always an exothermic process.

Two types of adsorption may be distinguished;
(a) PHYSICAL or Van der Waals^{ads} adsorption and (b) CHEMISORPTION. The degree of unsaturation of surfaces can vary considerably and, with those surfaces which are inert in the sense that the valency requirements of their atoms may be thought to be satisfied by bonding with adjacent atoms, adsorption takes place simply through forces of "physical adsorption". These

forces are similar to those causing the deviations of real gases from "ideal" behaviour, and in magnitude are of a similar order to those between molecules in a liquid. The heats of physical adsorption are not much larger, and are sometimes smaller, than the heats of condensation of molecules onto their own liquid or solid surfaces. In contrast, any interaction at the surface leading to changes in the energy states of electrons should be regarded as a chemisorption. This term implies formation of quasi-chemical bonds of the adsorbed substance with the solid surface. The heats of chemisorption are thus large in comparison with the heats of physical adsorption. Lennard-Jones¹ has demonstrated the contrast with extreme clarity in his classical work on potential energy changes during physical adsorption and chemisorption.

(11) Relevance of Adsorption Studies to Electrochemical Problems

In ordinary heterogeneous chemical reactions, the rôle of adsorption has been firmly established. In principle, electrochemical reactions are similar to chemical ones, since both involve interactions between particles having some kind of electrical charge or charge distribution. The practical difference, however, is that in electrochemical processes, some transfer of net charge occurs, usually at a metal-solution

interface, across a gradient of electrical potential. It is convenient to regard such transfers as usually involving a change of electrical as well as chemical free energy, and the total change of free energy is then termed the change of "electrochemical potential" by analogy with changes of chemical potential or Gibbs free energy in ordinary chemical processes. The term "electrochemical potential" (not to be confused with standard electrode potentials in the electrochemical series) was first defined and used by Butler² and Guggenheim.^{3,4}

The dependence of the kinetics of electrode processes on the structure of the interfacial electrical double layer and on the concentration of ions and molecules adsorbed at the electrode-solution interface cannot be over-emphasised. The importance of this dependence arises not only because the rates of electrode reactions are determined by the surface concentration of reactants (as in heterogeneous catalysis), but also because they are often dependent upon the energy of adsorption of the reacting species at the electrode surface. The distribution of potential in the electrical double layer and the adsorption of ions affect the rates of electrochemical reactions in two ways; firstly by determining the surface concentrations of ions available for reaction; and secondly by determining the potential drop at the interface across which the reacting adsorbed ions (or electrons) must pass in order to reach the transition state

of the reaction from its initial state. In some instances the electrode process may be affected both by the adsorption of the reactant and the reaction product.⁵ The adsorbed material, by changing the structure of the double layer, may alter the kinetic parameters of the reaction. Theories concerned with the structure of, and potential distribution in, the double layer at electrodes will hence be examined in some detail.

B. THEORIES OF THE ELECTRICAL DOUBLE LAYER

(1) Definitions

Very simply, the electrical double layer is an array of charged particles and oriented dipoles which exist at an interface. Its existence may arise in any of the five following ways: (1) a charge separation at the interface, usually resulting from charge transfer; (2) unequal adsorption of ions; (3) orientation of solvent molecules; (4) electron overlap; (5) charge separation by polarisation in the electrode field. Apart from its intrinsic interest, a knowledge of the structure of the double layer is a prime requisite for a more detailed interpretation of the kinetics of electrode reactions. In this discussion, consideration will be limited to the double layer at the interface between a metal and an electrolytic solution. The term "electrical double layer" will be retained despite recommendations to the contrary suggested at the Eighth

Meeting of the International Committee of Electrochemical Thermodynamics and Kinetics held at Madrid in 1956.⁶ This commission proposed that the term "electrochemical double layer" should be used in place of "electrical double layer," and in particular in place of "electrolytic double layer", an expression frequently employed in the German literature. The replacement of the latter description appears to be reasonable but no obvious advantage seems to be gained by adopting the first suggestion.

(ii) Qualitative Comparison between Existing Theories

Helmholtz⁷ regarded the double layer as equivalent to a condenser of constant capacity, i.e. with equal charges on the metal and in the solution facing each other at a constant distance. Helmholtz's treatment gives rise to a plausible value for the thickness of the double layer but does not take into account the thermal equilibrium between particles adsorbed in the double layer and those in the bulk of the solution. It is therefore necessary that the concept of a rigid double layer be replaced by one of a boundary layer, the structure of which can change with solution concentration.

Gouy^{8,9} took into account the fact that there must be equilibrium between the electrical forces which are responsible for the existence of the double layer and the osmotic forces tending to maintain homogeneity, and pointed

out that the ions could not be concentrated at a definite distance from the surface in a compact layer.

Chapman¹⁰ extended Gouy's conception of the double layer by introducing Poisson's equation to find the equilibrium distribution of ions in the diffuse double layer and the corresponding variation of electrical potential. His calculations were similar to those of Debye and Hückel to determine the distribution of ions in the ionic atmosphere around a given ion. The Gouy-Chapman theory leads to results incompatible with experimental work, in particular to completely erroneous values of the double layer capacity. The model also does not take into account the finite size of ions. The Gouy-Chapman theory also fails in another way because it does not take into account the reduction of the bulk dielectric constant value in the double layer due to dielectric saturation in the vicinity of the electrode as considered more recently by Conway, Bockris and Ammar¹¹ and by Grahame.^{12,13}

Stern¹⁴ avoided some of the above-mentioned difficulties by introducing two new postulates: (a) that ions could only approach the surface to some limiting distance corresponding to their finite effective radii in solution; and (b) that the ions may or may not be chemisorbed (or "specifically" adsorbed) at the interface. The first layer of ions adsorbed directly at the metal then constitutes a layer analogous to that suggested by Helmholtz but beyond this layer, the ions were regarded as

diffusely distributed as in the Gouy-Chapman theory. At the first layer in the Stern theory, the charges are regarded as associated with the Freundlich¹⁵ or ζ -potential, and the electrokinetic phenomena in electrolytes in contact with an interface are therefore due to effects connected with this mobile or diffuse portion of the double layer. The zeta potential may be defined as the potential at the surface of shear (e.g. between solid particles and the dispersion medium in electrophoresis) due to the combined effects of the charges on the surface and the equal and opposite ones of the ionic atmosphere. The zeta potential is not necessarily equal to the potential at the first layer of adsorbed ions (Figure 1c, page 9) since the hydrodynamic limit of shear at the interface is unknown. However, experimental zeta potentials¹⁶ and those calculated from the Stern theory are usually quite comparable.

In the Stern model the interfacial potential contains two components corresponding to separate potentials across the Helmholtz and diffuse layers. Since these components may be of opposite sign, two types of the Stern double layer may be sketched (see Figure 1c and 1d, page 9). It may be noted that, formally speaking, a transition from one type of Stern double layer to the other involves a state in which the double layer is wholly of a Helmholtz type. The usefulness of the Stern concept as a working hypothesis for the structure of the double layer has been examined at length by Grahame¹⁷ who developed the theory

Figure I. The Electrical Double Layer

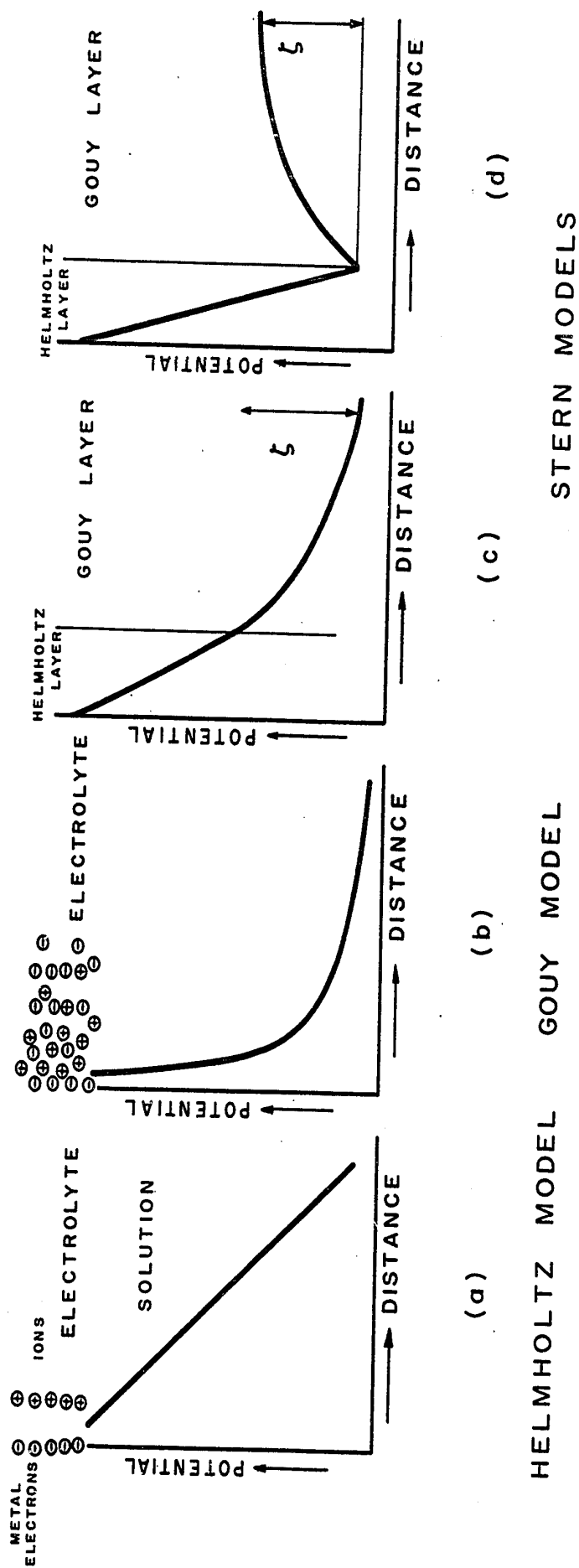
(a) Helmholtz Model

(b) Gouy Model

(c) Stern Model

(d) Stern Model

FIGURE I



further in terms of the finite size of ions and considered specifically the effects of taking into account the different degrees of solvation of anions and cations in the double layer.

Figure II a (page 11) illustrates some of the essential modifications made to the theory of the electrical double layer by Grahame. It depicts a very simple molecular picture of the electrolytic side of the interface. The closeness of approach of ions in the electrolyte to the metal surface is determined by whether or not their hydration shells can be displaced or distorted on the side nearest to the metal. Ions which do so as they approach the metal surface enter what is called the "Inner Helmholtz Layer". Ions which retain at least the first layer of their hydration shells cannot approach the electrode as closely, and the locus of their centres at closest approach is termed the "Outer Helmholtz Layer or Gouy Plane". Generally it has been assumed that the distribution of ions on the electrolytic side of the interface is determined only by electrical forces, although Stern recognised the possibility of "specific adsorption" forces. Grahame's work suggests that the distribution of ions in the diffuse part of the double layer can be regarded as determined only by the general electrical field but that ions occupying the inner Helmholtz layer must be regarded as adsorbed to the metal surface with some degree of chemical bonding and consequent distortion of their primary solvation sheath.¹⁸

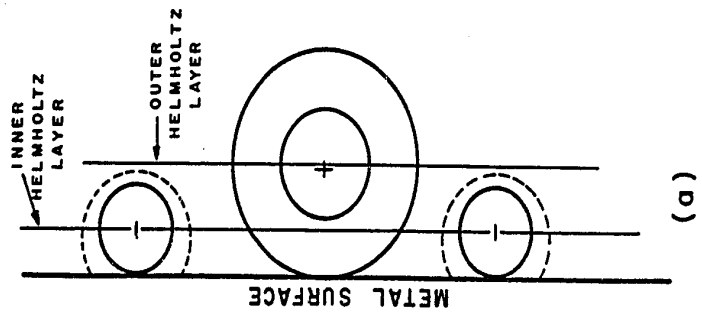
Figure II. The Electrical Double Layer

(a) Molecular Model

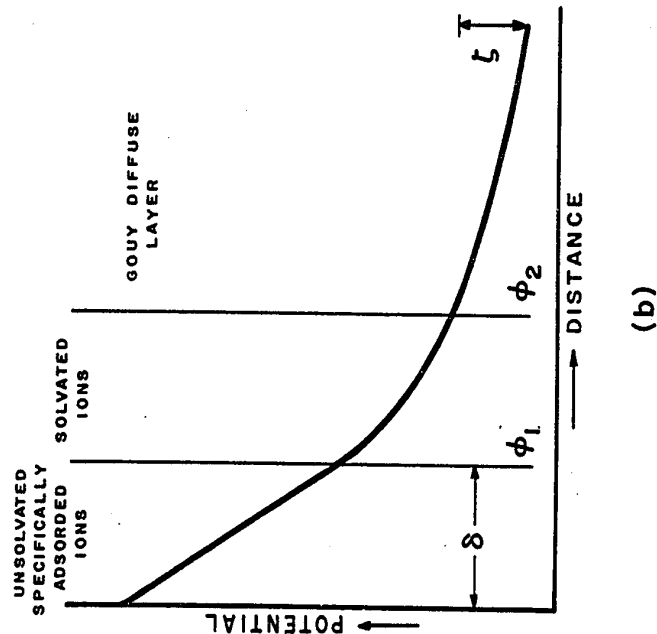
(b) Devanathan's Model

(c) Regions of the Double Layer.

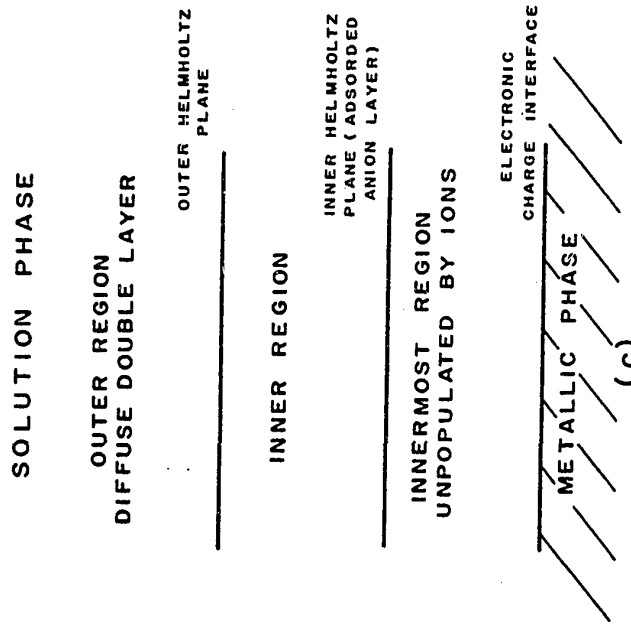
FIGURE II



MOLECULAR PICTURE
OF THE DOUBLE LAYER



DEVANATHAN'S MODEL



REGIONS OF THE DOUBLE LAYER

Grahame¹⁹ stressed that (a) ions "in contact" with the interface are found not to be separated from the metal by a layer of solvent, and (b) the electrical centres of anions are able to approach the interface more closely than the electrical centres of cations. The detailed structure of the electrical double layer at a metallic surface proposed by Grahame (see Figure II c, page 11) contains four distinct regions (i) the metallic phase upon whose surface an excess or deficiency of electrons may reside (ii) an "innermost" region lying next to the metallic phase and into which the electrical centres of ions cannot move because of their physical "crystallographic" size (iii) an "inner" region accessible to the electrical centres of anions but not of hydrated cations and (iv) an "outer" region containing a diffuse double layer of the type described by Gouy and Chapman, and limited at the electrode side by a plane at a distance equal to the average radius of the hydrated cations populating the double layer. The layer of anions is called the "adsorbed layer" because it is held at the inner Helmholtz plane not by simple coulombic forces but by short-range forces; the resulting adsorption being then termed "specific adsorption".

The first important point of difference between Grahame's and Stern's theories is the identification of the two planes, the inner and the outer Helmholtz planes, instead

of one. Stern did mention the possibility that such a breakdown might be necessary but did not recognise the importance of it. The necessity is shown by the fact that one cannot account for the amount by which the potential of the electrocapillary maximum (e.c.m.) of mercury (q.v. section E on the theory of electrocapillarity) is shifted by the adsorption of negative ions. The shift in the e.c.m. potential of mercury can be calculated unequivocally from Stern's theory, but the results are of the wrong ~~order of~~ magnitude, and change with concentration in a manner at variance with observation. The difficulty arises from the assumption, implicit in Stern's theory, that the inner and outer Helmholtz planes have the same potential. Grahame examined the shift of the e.c.m. potential of mercury caused by the adsorption of KCl , KCN , NaBr , KBr , CaBr_2 , NaNO_3 , KNO_3 , KI and $\text{K}_2\text{S}_2\text{O}_8$. In every case the observed value of the shift of potential is greater than the calculated one, indicating that the adsorbed ions (anions) are able to move in closer to the interface than cations. The second important difference between Grahame's theory and that of Stern is that only the layer of ions existing at the innermost boundary (inner Helmholtz plane) is regarded as held by short-range forces. Stern's theory, on the other hand, involves a layer at the surface which can contain both

positive and negative ions.

Devanathan²⁰ has developed the concept of the double layer further. He postulated the structure shown in Figure II b (page 11), which is substantially identical to that proposed by Grahame. The original Helmholtz layer is shown to be a duplex structure of solvated and unsolvated ions, while the diffuse layer remained essentially the same as before. The quantity " δ " is the distance between the centres of the specifically adsorbed ions from the metal surface and is characteristic of the nature of the ion. From the foregoing discussion it will be seen that modern descriptions of the structure of the electrical double layer suggest that it should, in fact, be more precisely called an electrical "triple layer".

(iii) Quantitative Comparison of Double Layer Theories

(a) The treatment of Helmholtz

The double layer is considered to be equivalent to a fixed parallel plate condenser of capacity C , where

$$C = q_m / \delta = E / 4 \pi \delta \quad (1)$$

and

$$q_m = E \delta / 4 \pi \quad (2)$$

q_m is the charge per unit area metal surface and ϕ is the metal solution potential drop; δ is the thickness of the double layer measured in terms of the mean distances of ion centres from the metal; ϵ is the dielectric "constant"¹⁰ of the solvent in the double layer.

(b) First approximation: The Gouy-Chapman theory for point charge ions.

Let n_0 be the average concentration of ions in the bulk of the solution, and W_x be the electrostatic work done in bringing the ions of one type from the solution to a point at a distance x from the electrode surface. Hence according

¹⁰ ϵ is sometimes referred to as the differential dielectric coefficient because it varies with field strength F . The problem of dielectric saturation still presents some difficulty in the theories of the double layer. The dielectric constant of the solvent has been assumed to be constant in the theory of Stern. This assumption is made in spite of the large electrical field present and the question arises whether or not this fact invalidates the theory. In order to resolve this issue Conway, Bockris and Ammar¹¹ have studied the dependence of ϵ as a function of F . Grahame^{12,13} also devised a comparable semi-empirical equation for ϵ as a function of F which was based on a theoretical treatment given by Booth¹⁴. Both groups of workers concluded independently that although ϵ falls to low values in the diffuse part of the double layer, the measurable properties of the double layer are not significantly affected. This conclusion was later borne out by experiment.²²

to the Maxwell-Boltzmann Law

$$n_x = n_0 \exp (-W_x/kT) \quad (3)$$

where n_x is the concentration of ions at x . The charge density at x is ρ_x and is given by the following expression

$$\rho_x = \sum n_0 z e \exp (-W_x/kT) \quad (4)$$

where the charge on an ion is ze (e is the electronic charge and z represents the valency).

The general relation between the electrical potential ϕ_x and the charge density at a point x is given by the Poisson equation

$$-\text{div} [E_x \text{ grad } \phi_x] = 4\pi \rho_x \quad (5)$$

which then reduces to the one dimensional form

$$-\frac{\partial (E_x \frac{\partial \phi_x}{\partial x})}{\partial x} = 4\pi \rho_x \quad (6)$$

where E_x is the dielectric constant at a distance x from the electrode. Introducing (4) into (6) the following relationship may be obtained

$$-\frac{\partial}{\partial x} (E_x \frac{\partial \phi_x}{\partial x}) = 4\pi e \sum z n_0 \exp (-W_x/kT) \quad (7)$$

(7) may be integrated directly using the two following assumptions: - (a) that the dielectric constant has a mean constant value $\bar{E}$ over the diffuse double layer and (b) that

U_x is simply an electrostatic term, dependent on the valency and not on the nature of the ion i.e.

$$U_x = ze (\phi_x - \phi_s) \quad (8)$$

where ϕ_s is the potential in the bulk of the solution.

Using the identity

$$\frac{\partial^2 \phi_x}{\partial x^2} = \frac{1}{2} \frac{\partial}{\partial \phi_x} \left(\frac{\partial \phi_x}{\partial x} \right)^2 \quad (9)$$

we obtain the equation for the ion distribution in the following manner:

$$\frac{\partial}{\partial \phi_x} \left(\frac{\partial \phi_x}{\partial x} \right)^2 = \frac{8\pi e}{\epsilon} \sum n_o z \exp \left[-ze(\phi_x - \phi_s)/kT \right] \quad (10)$$

Integrating (10) we obtain

$$\frac{\partial \phi_x}{\partial x} = \pm \left[\frac{8\pi kT}{\epsilon} \sum n_o \left\{ \exp \left(\frac{-ze(\phi_x - \phi_s)}{kT} \right) - 1 \right\}^{1/2} \right] \quad (11)$$

The figure unity occurs in equation (11) because the constant of integration must be evaluated and this is obtained by examining the result for the boundary condition: $\phi_x \rightarrow \phi_s$ as $x \rightarrow \infty$. The surface charge q_M can then be related to the field close to the interface by Gauss's Theorem.

$$\left(\frac{\partial \phi_x}{\partial x} \right)_a = \frac{-4\pi q_M}{\epsilon_s} \quad (12)$$

where a is the distance of closest approach of ions to the surface and ϵ_s represents the dielectric constant within

this distance.

Rearranging (12) we have

$$4 \pi q_M = -E_a \left(\frac{\partial \phi_x}{\partial x} \right)_a \quad (13)$$

which is the field at the region of the first layer.

This field may be identified approximately with that given by the Poisson-Boltzmann equation, i.e.

$$-E_a \left(\frac{\partial \phi_x}{\partial x} \right)_a = E_a \left[\frac{8 \pi k T}{\epsilon} \sum n_0 \left\{ \exp(-ze [\phi_x - \phi_a]/kT - 1) \right\}^{1/2} \right] \quad (14)$$

ϕ_x refers to the position where the value of $x = a$ at the double layer. From (13) we see that

$$q_M = -E_a \left(\frac{\partial \phi_x}{\partial x} \right) / 4 \pi$$

and assuming that $E_a \approx \bar{E}$ we arrive at the following

$$q_M = \pm \left[\frac{kT \bar{E}}{2 \pi} \sum n_0 \left\{ \exp(-ze [\phi_a - \phi_s]/kT - 1) \right\}^{1/2} \right] \quad (15)$$

With a $z=2$ valent electrolyte, $n_+ = n_- = n$, so that q_M can then be simplified to the following

$$q_M = \left(\frac{2 kT n \bar{E}}{\pi} \right)^{1/2} \sinh [ze (\phi_a - \phi_s)] / 2 kT \quad (16)$$

Both Gouy and Chapman identified ϕ_a with the potential at the metallic surface, i.e. $a = 0$, implying therefore that the ions were point charges. Experimental measurements contradict this assumption, as may be seen by reference to calculated and experimental capacities of the double layer.

The capacity of the double layer may be obtained by differentiating q_M with respect to potential, i.e.,

$$\frac{\partial q_M}{\partial (\phi_2 - \phi_s)} = C = \frac{\partial q_M}{\partial E_{(exp)}}$$

where C represents capacity and $E_{(exp)}$ refers to the experimentally measured potential. Thus we may obtain

$$C = \left(\frac{z^2 e^2 n}{2 \pi kT} \right)^{1/2} \cosh \left[ze (\phi_2 - \phi_s) / kT \right] \quad (17)$$

Grahame¹⁹ showed that the values of capacity calculated from (17) differed considerably from the observed capacities for a mercury electrode in four different aqueous solutions of sodium fluoride.

(c) Second Approximation: Ions of finite size

Better agreement with experiment is obtained by assuming that the ions have a finite size and that the plane of closest approach is at a distance x_2 from the electrode and has a potential ϕ_2 . The electrode-solution potential difference may be written as

$$\phi_M - \phi_s = (\phi_M - \phi_2) + (\phi_2 - \phi_s) \quad (18)$$

The capacity may now be written as follows;

$$\partial (\phi_M - \phi_s) / \partial q_M = 1/C = \partial (\phi_M - \phi_2) / \partial q_M + \partial (\phi_2 - \phi_s) / \partial q_M$$

and

$$\frac{1}{C} = \frac{1}{C_{M-2}} + \frac{1}{C_{2-s}} \quad (19)$$

In equation (17) we may now identify the term β_a with β_2 . Equations (17) and (19) may be solved for C whereupon

$$C = \frac{C_{M-2} \left(\frac{z^2 e^2 n F}{2 \pi kT} \right)^{1/2} \cosh \left[ze (\beta_2 - \beta_s)/2kT \right]}{C_{M-2} + \left(\frac{z^2 e^2 n F}{2 \pi kT} \right)^{1/2} \cosh \left[ze (\beta_2 - \beta_s)/2kT \right]} \quad (20)$$

Equation (20) may be simplified by writing

$$C = \frac{C_{M-2} \left(\frac{z^2 e^2 n F}{2 \pi kT} \right)^{1/2} \cosh \left[ze (\beta_2 - \beta_s)/2kT \right]}{C_{M-2} + C_{2-s}} \quad (21)$$

Two limiting cases may be examined for equation (21): -

(a) when $C_{M-2} \gg C_{2-s}$, then the overall capacity $C \approx C_{2-s}$ i.e.,

$$\left(\frac{z^2 e^2 n F}{2 \pi kT} \right)^{1/2} \cosh \left[ze (\beta_2 - \beta_s)/2kT \right] \quad (22)$$

This occurs when the solutions are moderately concentrated or when $\beta_2 - \beta_s$ is small.

(b) when $C_{2-s} \gg C_{M-2}$, then

$$C \approx C_{M-2} \quad (23)$$

Equation (23) is valid when $(\beta_2 - \beta_s)$ is large, i.e. when the double layer approximates to the Gouy model and the solutions are dilute. Calculated values of C from (21) do not agree well with experimental values. Frumkin²³ showed that better

agreement can be obtained if it is assumed that the C_{M-2} value is different when anions populate the compact layer from that when cations do so. Frumkin suggested the following equation

$$C_{M-2} = \frac{K_- \exp [e (\phi_2 - \phi_s)/kT] + K_+ \exp [-e (\phi_2 - \phi_s)/kT]}{\exp [e (\phi_2 - \phi_s)/kT] + \exp [-e (\phi_2 - \phi_s)/kT]} \quad (24)$$

where K_+ and K_- represent the contributions to the capacity of the electrode due to the cations and the anions, respectively.

In this treatment of the structure of the double layer, the capacity can depend on the nature of the ion only by an effect on the capacity C_{M-2} because, at a given value of q_M , C_{M-2} determines ϕ_2 and hence C_{2-s} . Differences in C_{M-2} might occur as a result of different distances of closest approach (λ_2) caused by the different sizes of the ions. These differences would be small, probably within a factor of two, and in fact it is found that in the absence of specific adsorption, the capacity curves are very similar for salts with cations of different types.

Another test of this theory can be made by comparing the calculated values of the "components of charge" in the diffuse double layer with experimental values for ions which are known not to be specifically adsorbed. In a solution of a 2-2 valent electrolyte the excess charge in the diffuse double layer due to cations in a lamina of thickness dx at a

distance x from the electrode is given by

$$ze (n_x^+ - n_s^+) dx = ze n_s [\exp (-ze (\phi_x - \phi_s)/kT) - 1] dx \quad (25)$$

where n_x^+ is the number of cations at a point x in the compact layer, n_s^+ is the bulk concentration as $x \rightarrow \infty$ and n_s is the average concentration of the ions in solution.

Integration of (25) gives the total excess charge

$$q_+ = \int_x^\infty ze n_s [\exp (-ze (\phi_x - \phi_s)/kT) - 1] dx \quad (26)$$

with the double layer starting at the outer Helmholtz plane ($\phi_x = \phi_2$); then

$$q_+ = (kT n_s E/2\pi)^{1/2} \exp (-ze (\phi_2 - \phi_s)/kT - 1) \quad (27)$$

Similarly we can obtain an expression for q_- . From electrocapillary measurements Γ_+ and Γ_- (the surface excesses) are obtained and in the absence of specific adsorption, q_+ and q_- may be equated to $z_+ e \Gamma_+$ and $z_- e \Gamma_-$, respectively. Experimental confirmation¹⁹ of this is satisfactory and lends support to the theory of the diffuse double layer outlined here.

Grahame¹⁹ studied the differential capacity of mercury in contact with aqueous sodium fluoride solutions as a function of concentration at 25° C. His results indicated that from the capacity measurements at any one concentration it was possible to calculate the capacity at all others. This result confirms that in the absence of specific adsorption

the differential capacity of the region lying between the metal and the outer Helmholtz plane depends upon the surface charge density on the metal and not upon the concentration of the electrolyte. The results not only serve as an additional confirmation of the classical theory of the diffuse double layer, but also can provide data which may be used as an exacting test of the accuracy of techniques used for the experimental measurements of the differential capacity of the electrical double layer.

(d) Third approximation: Specific adsorption of ions of finite size.

Stern's improvements to the theory of the structure of the metal - solution interface consisted of (1) allowance for the finite size of ions in their approach to the metal surface and (2) allowance for the "specific interaction" between the surface and the ions immediately adjacent to it. He assumed that the specifically adsorbed ions formed an ideal localized monolayer (at a position x_1 from the metal surface), and that the other adsorbed ions, which are not specifically adsorbed, formed a diffuse layer which could be described by the Gouy-Chapman equations. Specific interaction may be taken to signify interaction other than the electrostatic interaction of the ionic charge with the field due to the charge on the metal surface. More explicitly, an electrolyte

may be defined as specifically adsorbed at a mercury surface when the coordinates of the electrocapillary maximum are a function of the concentration of the electrolyte. At the e.c.m., q_M , the charge on the metal, is zero; hence there are no electrostatic forces² holding the ions to the surface.

It is now necessary to consider the charge in the compact double layer due to chemisorbed ions. In order to calculate this we require to use an adsorption isotherm. In Stern's model of the double layer x_2 becomes the distance at which specific forces are negligible, instead of the distance of closest approach (x_1) of the ions. The charge on the solution side of the double layer may be divided into two parts:

$$q_{1-2} + q_{2-s}$$

Furthermore,

$$q_M = -q_s = -(q_{1-2} + q_{2-s}) \quad (28)$$

and q_{2-s} may be obtained by using equation (15) whereby

$$q_{2-s} = (kT E_{2-s} / 2\pi) \sum n_x [\exp (-ze (\phi_2 - \phi_s) / kT) - 1]^{1/2} \quad (29)$$

The charge q_{1-2} within the boundary of the region where ions are

² It appears that small residual image forces should also be considered. However, the absence of specific adsorption of sodium fluoride at the e.c.m. implies that these forces are insignificant.

specifically adsorbed may be derived by a method analogous to that used by Langmuir²⁴ for a system where adsorption occurs on independent localised sites²⁵. Briefly, the charge per square centimetre on the specifically adsorbed layer is given by

$$q_{1-2} = \sum ze n_1 \quad (30)$$

and

$$n_1 = \frac{N_1}{\left[1 + \frac{N_s - n_s}{n_s} \exp(\Delta \bar{G}_{ads}^0/kT) \right]} \quad (31)$$

For dilute solutions when $N_s \gg n_s$, we have

$$\frac{n_s}{N_s - n_s} = \frac{n_s}{N_s} \approx x_s \quad (32)$$

For a binary electrolyte

$$q_{1-2} = ze n_1 \left[\frac{1}{1 + 1/x_s \exp(\Delta \bar{G}_{+ads}^0/kT)} + \frac{1}{1 + 1/x_s \exp(\Delta \bar{G}_{-ads}^0/kT)} \right] \quad (33)$$

where n_1 is the surface concentration of ions and n_s the volume concentration of ions. N_1 and N_s are the numbers of sites per square cm. on the surface and in the solution respectively. x_s denotes the mole fraction of the electrolyte in the bulk of the solution and $\Delta \bar{G}_{+ads}^0$ and $\Delta \bar{G}_{-ads}^0$ are the standard electrochemical free energies of adsorption for the cations and the anions, respectively.

Few quantitative tests of the Stern theory has been carried out. Philpot²⁶ demonstrated that the potential drop in the double layer occurs in two parts. Philpot made a plot of the charge density in the diffuse part of the double layer against the potential of the electrode surface and this revealed two nearly linear sections with different slopes joined by a non-linear section. This provides no information about Stern's theory of specific adsorption because the experimental results fit equally well a model in which only the finite size of the ions is taken into account. A second type of test^{17,27} is concerned with establishing whether the potential ϕ_1 in the specifically adsorbed layer and that ϕ_2 at the boundary of the diffuse double layer near the electrode are identical. Parsons²⁵ indicated that the two potentials are not equal.

One of the difficulties lies in the formulation of a precise definition of ϕ_1 . Stern assumed that in the absence of specific adsorption, $\Delta \bar{G}_{ads}^0$, the standard electrochemical free energy of adsorption, was simply the electrostatic free energy of adsorption of the ions of charge ze given by

$$\Delta \bar{G}_{ads}^0 = ze (\phi_1 - \phi_2) \quad (34)$$

Stern also assumed that $\phi_1 = \phi_2$ for the purpose of his calculations and showed (as expected) that the results obtained using these two assumptions differed little from

those obtained using the assumption $q_{1,2} = 0$. Theoretically β_1 cannot be equal to β_2 because the electric field between the layers 1 and 2 would be zero, unless the two layers were superimposed, i.e. $x_1 = x_2$. If the layers were superimposed, the ions which would contribute to $q_{1,2}$ would be in the first layer of the diffuse double layer and consequently their contribution to q_s would be estimated twice. Thus the assumption that $q_{1,2} = 0$ (i.e. when $\Delta \bar{C}_{ads}^0$ is large and positive) in the absence of specific adsorption is theoretically preferable, and simpler to use in calculations, than the assumptions $\Delta \bar{C}_{ads}^0 = 0$ and $\beta_1 = \beta_2$, although they lead to similar numerical results.

In the Stern treatment of specific adsorption, the isotherm chosen was equivalent to that of Langmuir, i.e. the specifically adsorbed ions were assumed to form an ideal localised monolayer in which there were negligible interactions between the adsorbed ions.²⁶ Parsons²⁹ used the experimental data obtained by Eain and Markov²⁷ and by Devanathan and Peries³⁰ for potassium iodide solutions to test the validity of using the Langmuir isotherm. These data are relevant since for the simple inorganic anions, the iodide ion is the most strongly adsorbed. Seven types of isotherms were compared with the experimental results: (i) An isotherm based on Henry's Law and corresponding to a film behaving like an ideal two-dimensional gas; (ii) the Freundlich isotherm;

(iii) the Langmuir isotherm; (iv) the Volmer isotherm; (v) an extended Volmer isotherm; (vi) Amagat's equation and (vii) a "square root" isotherm.

Parsons derived thermodynamical expressions for the surface excess at constant surface charge and these equations were integrated to obtain the effective surface pressure of a specifically adsorbed ionic film. Direct comparison of the effective pressure of an iodide film on mercury with the predictions of the seven isotherms showed that Stern's use of a Langmuir model is incorrect for such systems. Only two of the isotherms, namely (vi) and (vii) lead to agreement with experiment. Parsons' conclusions are not surprising since a Langmuir isotherm can give, only in some cases, a good semi-quantitative representation of the real adsorption behaviour; in many other cases it is inaccurate owing to the neglect of the interactions between similarly charged ions in the surface layer. From a physical viewpoint it is also easy to see that it is unlikely that there are localised sites on a liquid metal surface. Allowance for first order coulombic interactions in the adsorption of organic cations at the mercury electrode has been shown to give good agreements with experiment for the variation of $\Delta \bar{G}_{ads}^0$ over a range of surface coverage from 0 to 0.3.³¹ This matter is investigated further in the new experimental work reported in this thesis.

(e) The Eain and Markov effect²⁷

Rewriting equation (34) for the case of specific adsorption gives

$$\overline{\Delta G_{ads}^0} = \Delta G_{ads}^0 + ze(\phi_1 - \phi_s) \quad (35)$$

Stern wrote the basic electrostatic equation for the double layer in the form

$$K_{M-1}(\phi_M - \phi_1) = q_{1-2}^0 + q_{2-s}^0 = -q_M \quad (36)$$

where K_{M-1} is the integral capacity of the region $0 < x < x_1$ and is defined by this equation. At the electrocapillary maximum $q_M = 0$, so that

$$q_{1-2}^0 = -q_{2-s}^0 \quad (37)$$

and

$$\phi_M - \phi_1 = 0 \quad (38)$$

Equation (38) arises from an assumption that K_{M-1} cannot be zero. If (38) were correct, the difference in the potential of the e.c.m. in the presence of specific adsorption ($E_{ads}^{e.c.m.}$) from that in the absence of specific adsorption ($E_0^{e.c.m.}$) would be a measure of $\phi_1 - \phi_s$ in the former case, since $\phi_1 - \phi_s$ must be zero in the latter; i.e.

$$E_{ads}^{e.c.m.} - E_0^{e.c.m.} = \phi_1 - \phi_s \quad (39)$$

Eain and Markov showed that

$$(\phi_1 - \phi_s)^{e.c.m.} = \text{constant} + \beta \ln n_s^{\pm} \quad (40)$$

where n_s^- is the bulk concentration of a specifically adsorbed monovalent anion, and that $\beta \geq -kT/e$.
Therefore,

$$\frac{\partial(\beta_1 - \beta_2)}{\partial \ln n_s^-} \geq -kT/e \quad (41)$$

Experimentally it is found that for salts with specifically adsorbed anions

$$\partial(E_{ads}^{o.c.m.} - E_o^{o.c.m.}) / \partial \ln n_s^- < -kT/e \quad (42)$$

Equation (39) is hence invalid, and this is due to the neglect of (i) the discrete nature of the ionic charges; (ii) the dipolar double layer due to water orientation; and (iii) any potential difference arising from electron overlap at the metallic surface.

Eain and Markov pointed out that a plot of the $E^{o.c.m.}$ measured with respect to a constant reference potential was a linear function of the logarithm of the concentration for several electrolytes. The fact that the slope of this line was in excess of kT/e proved to be in direct conflict with Stern's formulation of the double layer theory. Grahame³² suggested that this be called the "Eain and Markov Effect" although these workers credited the idea to Frumkin.

The effect simply means that in the Stern theory, the forces of interaction between the adsorbed ions parallel to the interface are neglected. Then, as a result of the

mutual repulsion of such ions, they tend to arrange themselves in an hexagonal lattice^{33,34}, much distorted by thermal agitation. The work required to move an ion into such a lattice is much less than that calculated for an immobile smeared out charge of the same total magnitude, because the ions already make room for the incoming ion by separating and thus keeping at a distance from the incoming ion. Eain and Shikov³⁴ presented a mathematical formulation of the potential drop in the inner Helmholtz layer in terms of the discrete nature of the charge in the specifically adsorbed layer. Unfortunately their theory of discreteness of charge over-explained the experimental results obtained, that is to say, it predicted a larger anomaly than that observed. Fröhner³⁵, however, revised the theory by considering an hexagonally arranged lattice of adsorbed ions and obtained results in better agreement with experiment.

Recently Parsons³⁶ re-examined the Eain and Markov effect from a general thermodynamic standpoint. His results confirm the conclusion reached by Eain and Markov that the Stern theory is unable to account for the experimental results. Eain and Markov ascribed the discrepancy to Stern's neglect of the discrete nature of the specifically adsorbed charge. In contrast to this, Parsons attributed it to the use of an incorrect form of the adsorption isotherm. He showed that instead of the Langmuir model, two isotherms (1) one based on

the Amagat equation of state and (ii) one approximating to the Temkin isotherm^{37,38} were better in accord with the experimental results. In fact the latter isotherm gave somewhat better agreement with experiment than the former. The discreteness of charge effect has been re-investigated theoretically by Levine³⁹ who interpreted the effect in terms of the "self-atmosphere" energy U of the adsorbed anion, where U can be shown to be approximately proportional to the surface concentration of these ions. Although the approach is novel, Levine's results are substantially the same as those arrived at by Grahame.³³

C. ELECTRODE KINETICS AND THE ROLE OF ADSORPTION

(1) General Fundamental Considerations: Formulation of kinetic equations.

The formulation of kinetic equations for electrochemical reactions differs from that for ordinary homogeneous or heterogeneous reactions in the following ways;

(a) Rates can be measured and expressed in terms of current i which is directly proportional to the actual reaction velocity

v expressed, for example, as moles of product formed per second per square centimetre of electrode surface; thus

$$i = z F v \quad (43)$$

if z Faradays are involved in the production of one mole of product per second per square centimetre in, e.g., the forward direction of the reaction,

(b) The rate is not a unique function of concentration of reactants, temperature, surface conditions etc. but is dependent upon the electric potential difference across the interface at which the transfer of charge occurs. Since the reactants are charged and the final products usually uncharged or dipolar, there can be a variation of electrochemical potential of the initial state of the reaction (ions in solution at the interface, electrons in the metal) with the absolute electrical metal-solution potential difference $\Delta \phi$ at the interface. This causes a variation of the standard electrochemical free energy of activation $\Delta G^\ddagger$ with $\Delta \phi$ as expressed below.⁴⁰ Generally, for a z -electron charge transfer process,

$$\Delta G^\ddagger = \Delta G^\ddagger_0 + z\beta(\Delta\phi - \zeta)F \quad (14)$$

where $\Delta\phi - \zeta (= \Delta V)$ is the potential difference between the metal and the layer of adsorbed ions about to undergo reaction, ζ the potential of this layer with respect to that of the bulk of the solution and β is a factor (usually ca. 0.5) determined by the symmetry of the potential energy barrier for the electrochemical charge-transfer reaction and indicates approximately that fraction of ΔV through which charge must be transferred to reach the transition state from the initial state of the reaction. $\Delta G^\ddagger_0$ is the value of the free energy of activation when $\Delta V = 0$.

(c) The activity of reactant ions at the interface must be expressed in terms of the activity in the bulk.⁴¹ This is analogous to the case of heterogeneous reactions where the bulk and surface concentrations must be related through e.g. a Langmuir or Temkin isotherm, the conditions of pressure or concentration then determining in part the kinetic order of the reaction. Usually we can write for ions

j, an electrostatic isotherm of the form

$$(a_j)_{\text{surface}} = x(a_j)_{\text{bulk}} e^{-z \zeta F/RT} \quad (45)$$

where $z \zeta F$ is the difference of electrostatic free energy of the ions in the bulk and in the adsorbed layer at the surface, x is the thickness of the adsorbed layer and normalises the difference of units used for expressing the surface and the bulk activities.

In the case of specifically adsorbed ions, for which $(a_j)_{\text{surface}} \neq (a_j)_{\text{bulk}}$ when $\zeta = 0$, other "chemical" free energy factors enter into the determination of the electrochemical free energy of adsorption but there is no advantage, in principle, in distinguishing between the chemical and electrostatic factors in adsorption of the ions nor is such a distinction possible except at the e.c.m. of the metal.

(d) The terms in equations (43), (44) and (45) may be combined to give the basic kinetic equation for the current i as

$$i = \frac{zF kT}{h} \tau (a_j)_{\text{surface}} (1 - \theta) \exp \left\{ - [\Delta G^\ddagger + zF \Delta \phi - \zeta F] / RT \right\} \quad (46)$$

where θ is the fraction of the metal surface covered with products of the ionic discharge and other terms not previously defined have their usual significance.^{42,43} It will be noted that i is determined by θ and ΔV in addition to the factors noted. The latter term is not, in principle, determinable since it refers to an absolute single potential difference between two phases. In certain cases θ can be estimated from galvanostatic d.c. charging or discharging curves,⁴⁴ in limiting cases it may tend to zero or unity.

The problem of the inaccessibility of $\Delta \phi$ is usually avoided by expressing equation (46) in terms of the overpotential η where $\eta = \Delta \phi - \Delta \phi_r$ (47)

and $\Delta \phi_r$ is that value of $\Delta \phi$ at the interface when the reaction occurring there is in thermodynamic equilibrium. The rate can then be written as

$$i = \left\{ \frac{zF kT}{h} \tau \exp \left[-z\beta F \Delta \phi_r / RT \right] \right\} (a_j)_{\text{bulk}} (1 - \theta) \exp \left[-z \zeta F (1 - \beta) / RT \right] \exp \left[-\beta z F \eta / RT \right] \exp \left[-\Delta G^\ddagger / RT \right] \quad (48)$$

For a given metal and temperature, the terms inside the curly bracket are a constant K but $\Delta \phi_r$ is strictly still unknown.

The current i (or i_0 when $\eta = 0$) can, however, be easily measured and is an exponential function (the Tafel⁴⁷ equation) of η as indicated by equation (46).

(ii) Experimental Studies of the Effects of Adsorption on the Kinetics of Various Electrode Reactions

In order to keep this introductory review to a manageable size, only a representative choice of the many papers in this field will be discussed. Generally, the results of the experimental studies of pH and salt effects on hydrogen overpotential are in fair agreement with theory, and the best agreement is shown for metals exhibiting high hydrogen overpotential. Accurate data on the pH and salt effects in the hydrogen evolution reaction at mercury electrodes have been reported.⁴⁶⁻⁴⁹ On mercury and lead, the hydrogen overpotential is independent of pH up to solutions of about 0.1 N, but at higher concentrations some decrease in overpotential occurs.

For metals of low overpotential, e.g. nickel, platinum and silver [where the potential of the zero point (cf. e.c.m. of Hg) is nearer the reversible hydrogen potential than in the case of mercury or lead], the dependence on concentration begins at about 0.001 N, overpotential decreasing with increase of concentration. Salts decrease the hydrogen evolution rate at a given overpotential in dilute solutions

of constant pH, and increase the dependence upon pH, thus indicating that effects on the structure of the diffuse double layer are still of importance.

Much of the discrepancy between theory and experiment at intermediate and higher electrolyte concentrations observed in earlier experiments can be eliminated when calculations are made using an accurate solution of the Stern equation.⁵⁰ Other discrepancies arise from the neglect of the specific adsorption of anions and possibly of cations at the transition metals.

The variation of hydrogen overpotential at constant current density with changes of the concentration of H^+ in solution gives direct information concerning the question of whether hydrogen ions take part directly in the rate-determining process or not, and also related matters concerned with the structure of the double layer. Variation of the concentration of neutral salts affects the relation between the concentration of hydrogen ions in the bulk of the solution and that at the cathode-solution interface, and consequently addition of neutral salts can affect the velocity of the discharge reaction. Processes involving adsorbed H atoms will not be discussed here since the above has been presented in order to illustrate the importance and value of the study of effects concerned with the structure of the double layer and the adsorption of reacting ions.

Measurements of the differential capacity [q.v. section C (iv)] of the electrical double layer have been found useful in the elucidation of the kinetics of adsorption and desorption, particularly at the mercury-solution interface. Notable contributions include work by Frumkin and Melik-Gaikazyan^{51,53} on inference of adsorption kinetics from the frequency dependence in a.c. measurements of the double layer capacitance. Frumkin and Melik-Gaikazyan showed that the adsorption of normal aliphatic alcohols on mercury is always rapid compared with their diffusion to the electrode surface. Generally little work has been done on the kinetics of adsorption of organic materials on electrodes, but it is known that the process is diffusion controlled for aliphatic alcohols at mercury.⁵

The dependence of the kinetics of electrode processes on the structure of the interfacial double layer is especially pronounced in the case of electro-reduction of anions on a negatively charged surface. This has been stressed in a recent paper by Frumkin and his co-workers,⁵⁴ which contains an excellent summary of Russian contributions to this field of study. The rate of the electrode process depends on the interaction between the charge of the anion with the charges of the metal surface, and on its interaction with the charge of a neighbouring cation, which facilitates its approach to the negatively charged surface. Frumkin calls this effect the formation of "cationic bridges".

Frankin and Kalish⁵⁵ found that the rate of the persulphate electro-reduction on positively charged^{*} mercury surfaces decreases in the presence of anionic surface active agents. For example, when potassium bromide is used, the bromide ions are preferentially adsorbed, and this decreases the surface concentration of $S_2O_8^{2-}$ ions. Kalish and Frankin also reported that with a negatively charged mercury surface, the order of the effectiveness of halogen ions is reversed, and the current strength at a given potential then increases in the order $Cl^- < Br^- < I^-$. The small adsorption of anions which occurs on a negatively charged surface exerts an influence on the kinetics of the process opposite to that observed in the case of the strong adsorption on a positively charged surface. A further result is that the acceleration of the $S_2O_8^{2-}$ electro-reduction by iodide ions is found to depend on the nature of the cations, increasing in the order $Na^+ > K^+ > Ca^+$.

An interesting example of the influence of adsorbed substances on the kinetics of an electrode process has been reported by Frankin and his co-workers⁵⁶ who followed the adsorption of hexyl alcohol at mercury by means of both electrocapillary measurements and double layer capacity measurements.

^{*} i.e. on the anodic branch of the electrocapillary curve.

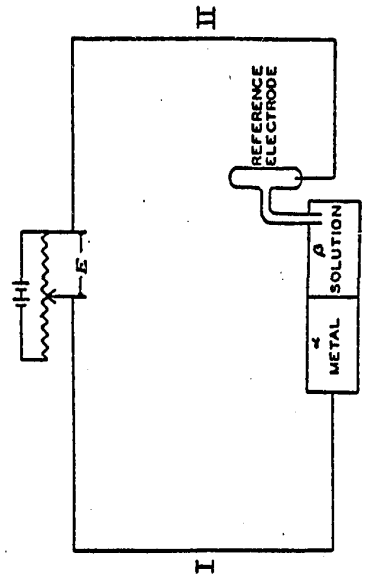
Tafel polarisation lines [i.e. plots of e.m.f. (E_H) versus log current density (i)] for hydrogen evolution were also determined in the same solutions. With hexyl alcohol, Frumkin showed that although the Tafel relationship ($\eta = a - b \log i$) still holds in the presence of the adsorbed layer, both constants 'a' and 'b' are affected. The observed increase of hydrogen overvoltage vanishes as would be expected at the potential of -0.8 v. where the capacity and electrocapillary data indicate desorption of the additive (see Figure III (a) page 42 cf. plots marked 3 and 4). In the case of hydrogen evolution on mercury from hydrochloric acid solutions in the presence of fatty acids, the influence of adsorbed layers is limited to an increase of the constant 'a',⁵⁷ which means that the mechanism of the process remains essentially the same in the presence of the organic substance as in its absence but that its rate is diminished.

The retarding action of potassium chloride and barium chloride on the ^{rate of} hydrogen evolution at a mercury electrode from a dilute solution of hydrochloric acid has been explained by Frumkin⁵⁸ as due to the shift of the β_1 potential (i.e. the potential at the distance of closest approach to the electrode surface) towards less negative values. Furthermore, organic cations, like $N(C_4H_9)_4^+$, shift the β_1 potential towards positive values, and strongly inhibit the discharge of Zn^{2+} or Cd^{2+} at zinc/amalgam and Cd/amalgam electrodes. It also inhibits the

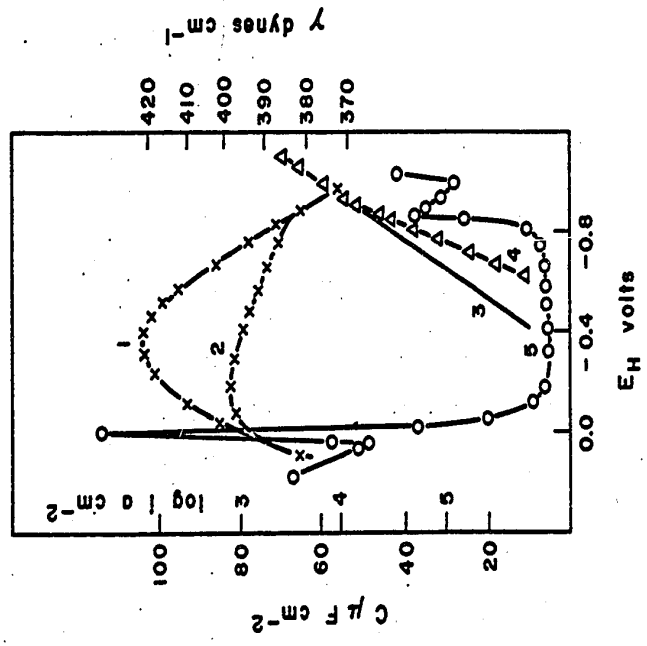
Figure III.

- (a) 1 and 2 represent electrocapillary curves for the base solution and the solution containing hexyl alcohol. Curves 3 and 4 show the Tafel polarisation lines before and after, respectively, addition of hexyl alcohol. Curve 5 shows the behaviour of the double layer capacity.
- (b) Schematic balanced circuit representing the system used for deriving the thermodynamic equations in the theory of electrocapillarity.

(b)



(a)



discharge of H^+ on mercury and lead electrodes,⁵⁹ but accelerates the discharge of persulphate anions.⁶⁰ The effect on the cathodic reaction arises presumably because of repulsion of the reacting cations out of the double layer owing to excess positive charge arising from the specifically adsorbed cations. Direct evidence for this type of effect with regard to H^+ ions and methyl pyridinium ions is given in subsequent sections of this thesis.

Adsorption of a mixture of two substances has an interesting effect when the more strongly adsorbed substance (gelatin) is less effective than the other substance (camphor) in making the electrode reaction more reversible $[Cd^{2+}/Cd(Hg)]$. Thus Sagaynova and Stromberg⁶¹ showed in these competitive adsorption experiments that the addition of gelatin to a solution of Cd^{2+} ions containing camphor decreases the overvoltage because of displacement of the camphor by gelatin. The exchange current (defined as the current density pertaining to either direction of the overall electrode reaction at reversible equilibrium) is thereby raised. Direct electrocapillary studies of competitive adsorption was first made by Butler and Okrent.⁶²

The effect of adsorption of certain alkaloids and amines on hydrogen overvoltage is peculiar in that the overvoltage may be increased or decreased. Two competitive effects are involved: (1) increase in overvoltage because of adsorption

of the alkaloid and (2) decrease in overvoltage because the alkaloid is a better proton donor than H_3O^+ . A detailed analysis of these effects at the stationary Hg electrode was made by Conway, Beckris and Lovrocek⁶³ using quinine, narcotine and morphine; the effects of these substances on the kinetics of the hydrogen evolution reaction at mercury were examined and related directly to the adsorption of the compounds determined by electrocapillary measurements. The more rapid proton transfer from the alkaloid ions than from H_3O^+ arises because the heat of activation for proton transfer from nitrogen is less than from oxygen in H_3O^+ , and also because ~~the~~ the change of the potential in the Helmholtz layer, due to the adsorption of the alkaloid cation, modifies the rate of proton transfer at a given electrode potential. Inhibiting effects arise at high current densities when the proton transfer rate from H_3O^+ exceeds that from the adsorbed organic ions which become neutralised and then block the surface. Studies of adsorption of species involved in electrode reactions such as this are thus necessary for a complete understanding of the kinetics involved.

Finally, studies of the effect of specific adsorption of iodide ions on hydrogen overvoltage by Kolotyrkin⁶⁴ leads to some interesting new facts in the relationship between adsorption and electrode kinetics. Kolotyrkin examined the adsorption of

iodide ions on silver and lead electrodes using labelled ^{131}I . His results show that the adsorption of iodide ions on lead can bring about both an increase (surface coverage $\theta > 15\%$) as well as a decrease in hydrogen overvoltage ($\theta < 15\%$). In this way, lead occupies an intermediate position between silver and mercury. It had been shown by Joja⁶⁵ that the adsorption of iodide ions on mercury leads only to a decrease in hydrogen overvoltage. With silver, the dependence of hydrogen overvoltage on adsorption of iodide ions is opposite to that demonstrated for mercury. Kolotyrkin suggested that the difference in the behaviour of these metals arises from the fact that the process of hydrogen evolution can be influenced by the specifically adsorbed anions in two different ways. Firstly, the specific adsorption of anions can bring about a change in the electrical properties of the metal-solution boundary, particularly with regard to the distribution of the potential which can cause (a) an increase in the surface concentration of the reacting ions, and (b) changes in that part of the total potential difference upon which the energy of activation of the electrode reaction depends. The net result is thus a decrease in the hydrogen overvoltage. Secondly, the specific adsorption of iodide ions was regarded as leading to a change in the catalytic properties of the electrode surface and especially to a lessening of the energy of the metal-hydrogen bond which causes a decrease of rate of

the reaction and a corresponding increase of overvoltage. The experimentally observed changes in hydrogen overvoltage arise from the net effect of the two factors mentioned above. These results lend weight to the view expressed elsewhere (see Appendix) that the effects of additives on electrode reactions cannot be generalised and the effects observed will depend usually on the individual chemical properties of the additive and the properties of the electrode metal such as its potential of zero charge, and its electronic and adsorptive properties.

D. THERMODYNAMIC THEORIES OF ELECTROCAPILLARITY

(1) Definitions

The significance of the term "electrocapillarity" is not commonly well understood. It may be defined as the study of "ideal" polarised electrodes, and of electrodes which can behave almost like ideal polarised electrodes. The ideal polarised electrode is characterised by the existence of an electrostatic rather than an electrochemical equilibrium between the metal and the electrolyte phase. This equilibrium is analogous to that in a charged parallel plate condenser. Behaviour approximating to that of an ideal polarised electrode is observed only with high overvoltage metals. The importance of phenomena at such electrodes rests upon the fact that they

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can be treated by exact thermodynamic means.^{19,66} Experimentally the ideal polarised electrode is one which behaves like an electrical condenser without leakage. Its capacity arises from the fact that charges may approach or recede from it, but they do not cross it. This definition is, however, too strict ever to be fully realised in the laboratory but close approximations to it are possible, and what is more important, the deviations which are unavoidable have negligible effect*. A practical ideal polarised electrode must have a very low exchange current and an high Tafel 'b' value (loc. cit.), and operating conditions must be such that the potential of the electrode is kept sufficiently low that the rate of any electrode process occurring must be small, e.g. less than 10^{-3} amp per square centimetre.

(11) Electrocapillary Studies

Metal-solution interfaces lend themselves to the exact study of the double layer better than other types of interface because of the possibility of varying the potential difference between the phases without varying the composition of the solution. Mercury is pre-eminently suitable for electrocapillary studies as its surface tension is readily measurable. It is also distinguished by its low chemical reactivity and its

* cf. page 54.

high hydrogen overvoltage. The latter characteristic makes it possible to work at potentials which would otherwise be objectionable because of a rapid evolution of hydrogen from the reduction of components of the solution.

(iii) Electrocapillary Curves

The surface tension of mercury is strongly dependent on the electrode potential and hence the charge in the electrical double layer at its interface with an electrolyte. This means that if a mercury electrode is polarised by applying an e.m.f. to an electrolyte cell of which it forms part, the strength of the polarisation E influences the surface tension γ . The nature of this correlation between E and γ was first observed by Lippmann.^{67,68}

The surface tension of a liquid is a measure of the energy required per square centimetre (or the force per centimetre) to maintain the square centimetre in equilibrium with the residual attractive interaction potentials of atoms or molecules in its surface. If, as with mercury in an electrolyte, the metal surface carries with it an electrical double layer, the like charges comprising each side of the double layer repel one another, creating a force in opposition to the residual attractive forces mentioned above. It is to be expected therefore that the surface tension will be lowered by increasing the charge density (and consequently the electrode potential)

at a mercury surface. This lowering will take place whether mercury carries a positive or negative charge, and if adsorbed ions of different size could be considered to act only electrostatically without any specific chemical action themselves, we should expect the relationship between electrode potential and surface tension to be symmetrical about the maximum of the latter. If we plot the surface tension as ordinate and the potentials applied to the mercury as abscissae, the curve is called an electrocapillary curve. The usual form of this curve approximates to that of a parabola with its vertex uppermost.

At the maximum of the curve where $d\gamma/dE = 0$, the surface charge ' q_M ' = 0 as shown below, and the potential difference arising from excess ion and electron charge in the double layer is zero;⁶⁹ thus;

$$\frac{d\gamma}{dE} = -q_M = 0 \text{ at the e.c.m.} \quad (49)$$

The quantity q_M was identified by Helmholtz as numerically equal to the charge on each side of the double layer and the vertex of the curve is known as the electrocapillary maximum. Surface active anions⁶⁹ usually depress the left branch

⁶⁹ This does not imply that the total potential difference at the interface is zero when $q_M = 0$. This is not, in fact, to be expected since residual potential differences at the interface will exist due to dipole orientation and electron overlap or asymmetry at the boundary of the metal.

(positive with respect to the e.c.m.) of the curve, and surface active cations⁷⁰ depress the right-hand branch of the curve (i.e. negative with respect to the e.c.m.). Anions are increasingly adsorbed as the mercury becomes more positive, and cations as the mercury becomes more negative. The adsorption of aliphatic neutral organic molecules creates a truncation of the electrocapillary curve. This is caused by their preferential adsorption in the region of the e.c.m., and the extent of their adsorption is diminished by both positive and negative polarisation. More complex effects occur with aromatic and conjugated heterocyclic molecules and form the basis of studies reported later in this thesis.

(iv) Thermodynamic Theory: Ionic components of charge in the double layer.

Significance of charged components: The metallic phase is regarded formally as being composed of two charged components: electrons and metallic ions. The solution phase is considered to be composed of neutral solvent molecules and of ions of whatever sort may be present. These ions are the charged components of the solution phase. It is possible by thermodynamic means to ascertain not only the charge on a mercury surface in contact with an electrochemically inert electrolyte but also the components of charge in the solution side of the double layer. These components, called σ_+ and σ_- .

are the surface excesses¹¹ of cations and anions, respectively, in unit area of the double layer. The actual values of Γ_+ and Γ_- depend on the choice of a boundary to represent the surface. It is convenient and usual to define the interfacial plane such that $\Gamma_{\text{solvent}} = 0$. This arbitrary choice⁹ puts the selected boundary very close to the interface and gives rise to values of Γ_+ and Γ_- which have simple and precise thermodynamic meaning.

The thermodynamic equations for the ideal polarised electrode may be derived by reference to Figure III (b) (page 41) where α is the metallic phase of the ideal polarised electrode in contact with the solution β . The reference electrode contains electrolyte β , hence there is no liquid junction potential. ψ^I , ψ^{II} , ψ^α and ψ^β are the Volta or contact potentials of the several phases. Following Grahame,¹⁹ we may then write for the circuit [Figure III (b)] in balance

$$E + (\psi^\alpha - \psi^I) + (\psi^\beta - \psi^\alpha) + (\psi^{II} - \psi^\beta) = 0 \quad (50)$$

⁹ An alternative method of defining the Γ terms has been given by Guggenheim^{72,73} by expressing the surface excess of components as the concentrations per square centimetre in a surface phase of finite but small thickness e.g. equal to the thickness of the adsorbed molecules. This method, which is more elegant than that adopted by other workers, leads to the same thermodynamic results. [cf. Adam⁷⁴]

are the surface excesses⁷¹ of cations and anions, respectively, in unit area of the double layer. The actual values of Γ_+ and Γ_- depend on the choice of a boundary to represent the surface. It is convenient and usual to define the interfacial plane such that $\Gamma_{\text{solvent}} = 0$. This arbitrary choice^{*} puts the selected boundary very close to the interface and gives rise to values of Γ_+ and Γ_- which have simple and precise thermodynamic meaning.

The thermodynamic equations for the ideal polarised electrode may be derived by reference to Figure III (b) (page 41) where α is the metallic phase of the ideal polarised electrode in contact with the solution β . The reference electrode contains electrolyte β , hence there is no liquid junction potential. ψ^I , ψ^{II} , ψ^α and ψ^β are the Volta or contact potentials of the several phases. Following Grahame,¹⁹ we may then write for the circuit [Figure III (b)] in balance

$$E + (\psi^\alpha - \psi^I) + (\psi^\beta - \psi^\alpha) + (\psi^{II} - \psi^\beta) = 0 \quad (50)$$

^{*} An alternative method of defining the Γ terms has been given by Guggenheim^{72,73} by expressing the surface excess of components as the concentrations per square centimetre in a surface phase of finite but small thickness e.g. equal to the thickness of the adsorbed molecules. This method, which is more elegant than that adopted by other workers, leads to the same thermodynamic results. [cf. Adam⁷⁴]

E is the reading on the potentiometer and is equal to $(\psi^I - \psi^{II})$. In electrocapillary work E is often negative, is kept constant in composition so that $(\psi^\alpha - \psi^I)$ is constant. Therefore

$$d(\psi^\beta - \psi^\alpha) = -dE = d(\psi^{II} - \psi^\beta) \quad (51)$$

Introducing the well known Gibbs's adsorption equation^{74,75} in the following form for constant temperature and pressure

$$d\gamma = - \sum_i \Gamma_i d\bar{\mu}_i \quad (52)$$

Here $d\bar{\mu}_i$ is the change in electrochemical potential at constant temperature and pressure of a component i and $d\gamma$ is the corresponding change in surface tension. Γ_i represents the excess of i in moles per unit area of interface over that which would be present if each phase were of characteristic uniform composition up to a plane drawn parallel to, but not necessarily coincident with, the actual interface. By writing electrochemical potentials in terms of chemical potentials in equation (52) we can obtain the basic equation applicable to any ideal polarised electrode at constant temperature. It may be noted that an alternative derivation not involving electrochemical potentials has been given by Parsons,⁷⁶ but the same results ensue.

The formulation of the basic equation using (52) is as follows:

$$d\gamma = q_M d(\psi^\beta - \psi^\alpha) - \sum \Gamma_i d\mu_i \quad (53)$$

where μ_i represents the chemical potential or partial molar free energy and q_M is the net charge at the metal surface.

From equation (53) we can write

$$d\gamma = -q_M dE - q d(\psi^{II} - \psi^\beta) - \sum \Gamma_i' d\mu_i' \quad (54)$$

where $\sum \Gamma_i' d\mu_i'$ now includes components of the non-metallic phase.

Since we are considering the composition of the metallic phase to remain constant, the chemical potentials of the components of the phase are unchanged and $d\mu_i = 0$ for each of such components. Next, we consider the expression for q_M which is the total charge equal and opposite to that of the ions in the solution side of the double layer (q_s). Thus

$$q_M = -F \sum \Gamma_i z_i \quad (55)$$

This summation is limited to the ions of the non-metallic phase; F is the Faraday, and z_i is the valence of i including sign.

We may now consider the application of equation (54) to the ideal polarised electrode at constant metal and solution composition (and this is designated by the subscript $^\mu$). Each term in the summation is zero, and so also is $d(\psi^{II} - \psi^\beta)$, since the interface ($II = \beta$) is that at the reference electrode.

Therefore we arrive at

$$\frac{d\gamma}{dE} = -q_m \quad (56)$$

which is the Lippmann equation. It indicates that the slope of the electrocapillary curve is equal to the negative of the electric charge density on the surface of the metallic phase.

(v) Validity of the Thermodynamic Theory of Electrocapillarity

The application of Gibbs's equation to the problems of electrocapillarity has been subject to much dispute in the older literature. The difficulty has been partly associated with a failure to understand the properties of the ideal polarised electrode, which has been frequently confused with non-polarisable (reversible) electrodes, normally the subject of electrochemical thermodynamics. Grahame¹⁹ has discussed in detail the possible non-equilibrium factors involved in the use of mercury as a practical ideal polarised electrode. He showed that, except for hydrogen, only negligible quantities of reaction products may be obtained at equilibrium when mercury is polarized by applying an e.m.f. to an electrolyte cell of which it forms a part. If the pressure of hydrogen required for equilibrium is appreciable then it may be contended that charge would move from the mercury surface to the solution in the course of building up this equilibrium concentration. Under this condition, the mercury electrode would not meet the requirements of an ideal polarised electrode as previously defined. However, from a

practical point of view, the high hydrogen overvoltage at mercury causes the attainment of complete equilibrium to be very slow compared with the rate of attainment of ionic (electrostatic) equilibrium within the double layer (usually a matter of milliseconds or even microseconds). In all such cases the slow reaction may be ignored. Therefore we are justified in considering that the mercury electrode is a practical ideal polarised electrode.

A further difficulty has arisen because of the fact that polarised electrodes are seldom actually exactly at equilibrium, although this is a purely practical matter and influences the experimental results almost negligibly. The early treatments of this problem are characterised by an unnecessarily obscure point of view. Typical treatments are those of Frumkin,⁷⁷ Schofield⁷⁸ and Butler.⁷⁹ These authors have discussed the electrocapillary curves as though the relevant adsorption of species on the water side was confined to that of mercurous ions, although their equilibrium concentration must be vanishingly small in normal potassium chloride solutions. Koenig⁸⁰ pointed out that electrocapillary curves are more often than not obtained when no mercurous ions are present in the solution; indeed the condition for successful measurements is that there should be no ions common to both phases.

In the earlier literature the statement is encountered that the polarisation of the surface is set up by the transference of mercurous ions from the metal to the water. This does not seem to be correct because the double layer can be built up by the attraction or adsorption of any ions (or indeed even dipolar neutral molecules) that happen to be present in solution. The charge on the metal has been represented by an excess or deficiency of electrons on the metal side of the interface and the potential difference between the phases has been attributed to the differences of concentration of the mercurous ions. This is only correct under certain conditions and discussions of the adsorption of mercurous ions from the solution phase are generally unnecessary, though they may formally lead to the correct results for the charge on the surface [e.g. see reference (79)] .

Koenig made two rather improbable assumptions in his derivation of equations for electrocapillarity: (a) equilibrium does not subsist at the interface and (b) there exists at the interface a barrier impermeable to charged particles. In spite of these assumptions, his theory led to satisfactory results. This is not inconsistent because Grahame and Whitney⁸¹ have shown that ^{it} is unnecessary to retain either of Koenig's assumptions. Charged particles "fail" to cross the interface, not because of a lack of any thermodynamic tendency to do so but rather on account of the high

activation energy for their transfer, so that the double layer remains virtually undisturbed.

(vi) Effect of Varying the Composition of the Electrolyte

Here we note that the reference electrode must be chosen appropriately so that the potential difference $\psi^{II} - \psi^I$ does not include any liquid junction potentials. There are two possible types of electrodes which may be considered, those which are singly reversible to one of the anions (j^-) and those which are reversible to one of the cations (j^+). The observed e.m.f. E as read on the potentiometer will be E_j^- and E_j^+ , respectively. If the reference electrode is reversible to one of the anions then,

$$d\gamma = -q_M dE_j^- - \sum \Gamma_i d\mu_i - q_M d(\psi^{II} - \psi^I) \quad (57)$$

From this point onward it will be supposed that only one anionic and one cationic component are present. The surface of reference with respect to which Γ_i 's are referred will be chosen as usual such that $\Gamma_{\text{solvent}} = 0$. The presence of only a single anionic and a single cationic component makes the subscript j superfluous and the other superscripts obvious. Now if the reference electrode used is reversible to the anion, equation (57) becomes

$$d\gamma = -q_M dE^- - \Gamma_+ d\mu_+ - \Gamma_- d\mu_- - q_M d(\psi^{II} - \psi^I) \quad (58)$$

From the definition of chemical potential it follows that

$$d\mu = \nu_- d\mu_- + \nu_+ d\mu_+ \quad (59)$$

where μ is the chemical potential of the neutral salt, and ν_+ and ν_- are the numbers of cations and anions, respectively, formed by the dissociation of one molecule of salt.

The reversible potential ($\psi^{II} - \psi^I$) varies with the chemical potential of the anion according to the equation

$$z_- F d(\psi^{II} - \psi^I) = d\mu_- \quad (60)$$

From the definition of q_M , or from electroneutrality requirements,

$$q_M + z_+ F \Gamma_+ + z_- \Gamma_- F = 0; \quad (61)$$

when equations (59), (60) and (61) are introduced into equation (58), and noting that $z_+/z_- = -\nu_-/\nu_+$, the following simple and important result is obtained:

$$d\gamma = -q_M dE_- - \frac{\Gamma_+}{\nu_+} d\mu \quad (62)$$

If the reference electrode is reversible to the cation, one obtains by an analogous procedure

$$d\gamma = -q_M dE_+ - \frac{\Gamma_-}{\nu_-} d\mu \quad (63)$$

At constant composition, (62) and (63) reduce to the Lippmann equation.

At the e.c.m., when $q_M = 0$, we have

$$\frac{d\gamma_{\max}}{d\mu} = -\Gamma_-^{\max}/\nu_- = -\Gamma_+^{\max}/\nu_+ \quad (64)$$

The quantities on the right hand side of equation (64) are equal to $\Gamma_{\text{salt}}^{\text{max}}$, the number of moles of neutral salt adsorbed per unit area at the e.c.m. Hence

$$\frac{d\gamma^{\text{max}}}{d\mu} = -\Gamma_{\text{salt}}^{\text{max}} \quad (65)$$

At constant E_- or E_+ equations (61) and (62) become

$$-\gamma + \left(\frac{d\gamma}{d\mu}\right)_{E^-} = \Gamma_+ \quad (66)$$

and

$$-\gamma - \left(\frac{d\gamma}{d\mu}\right)_{E^+} = \Gamma_- \quad (67)$$

These results indicate that Γ_+ and Γ_- can be obtained at any point on the electrocapillary curve by measuring the rate of change of surface tension γ , with composition at constant potential E_- and E_+ , respectively. This derivation is thermodynamically rigorous. Very convenient alternate forms of (66) and (67) are obtained by dividing through by the Lippmann equation, namely

$$\frac{d\gamma}{dE_{\pm}} = -q_M \text{ (with } E_- \text{ or } E_+ \text{ for } E)$$

Hence we obtain

$$-\gamma + q_M \left(\frac{dE_{\pm}}{d\mu}\right) = \Gamma_+ \quad (68)$$

and

$$-\gamma - q_M \left(\frac{dE_{\pm}}{d\mu}\right) = \Gamma_- \quad (69)$$

It may be noted that components of charge can also be derived from direct differential capacity measurements by a.c. impedance techniques.⁶² Such capacity data (which are equivalent to values of dq/dE or $-d^2\gamma/dE^2$) can be easily measured. Thermodynamic evaluation of the components of charge, which are the quantities of interest in regard to adsorption and structure of the double layer, can only be carried out by reference to some electrocapillary data; the latter are required for determination of the necessary constants of integration. Most of the work of Grahame has been carried out by this kind of procedure using simple electrolyte solutions. In solutions of some organic solutes and at solid electrodes frequency dependence of the measured capacities can complicate the thermodynamic interpretation of the data. In the present work reported in this thesis, components of charge have been derived only from electrocapillary measurements.

E. THERMODYNAMICS OF ADSORPTION IN ORGANIC AMINE SYSTEMS

Thermodynamic studies of the adsorption of amine derivatives in acid solutions, where they exist predominantly in the form of the conjugate acid ions " $R \rightleftharpoons NH^+$ ", were first made by Conway, Bockris and Lovrocek⁶³ at the mercury electrode. Adsorption isotherms were obtained for several alkaloids in

hydrochloric acid solutions and their adsorption was quantitatively related to their catalytic effects on the hydrogen evolution reaction at mercury. Antropov⁸³ and Banerjee^{84,85} have made electrocapillary studies of some simpler bases in sulphuric acid solutions but have not analysed their data thermodynamically. Gierst et al⁸⁶ have examined the adsorption of (neutral) amines in neutral solutions by electrocapillary (drop weight technique) measurements.

Eckric and Blomgren³¹ have examined the application of Gibbs' equation to electrocapillary studies of various aromatic amines (RNH_2) on mercury in aqueous hydrochloric acid, in which the ratio of the concentrations of ionized amine (RNH_3^+) to that of the neutral amine molecules exceeds 10^3 . For such a system they wrote the Gibbs equation in the following manner:

$$d\gamma = e_s dE - \Gamma_{\text{H}_3\text{O}^+} d\mu_{\text{H}_3\text{O}^+} - \Gamma_{\text{Cl}^-} d\mu_{\text{Cl}^-} - \Gamma_{\text{RNH}_3^+} d\mu_{\text{RNH}_3^+} - \Gamma_{\text{RNH}_2} d\mu_{\text{RNH}_2} \quad (70)$$

Here Γ and μ terms represent the surface excess and chemical potentials of the indicated species and other terms are as defined previously.

The following relations are self evident:

$$d\mu_{H_3O^+} + d\mu_{Cl^-} = d\mu_{HCl} \quad (71)$$

$$d\mu_{H_3O^+} + d\mu_{RNH_2} = d\mu_{RNH_3^+} \quad (72)$$

If E_H is the potential of the mercury with respect to an hydrogen electrode in the aqueous HCl - amine solution.

$$dE = dE_H + \frac{1}{F} d\mu_{H_3O^+} \quad (73)$$

Furthermore,

$$q_s = F (\Gamma_{H_3O^+} + \Gamma_{RNH_3^+} - \Gamma_{Cl^-}) \quad (74)$$

From equations (70 - 74) we obtain the general equation

$$- \gamma = q_s dE_H - (\Gamma_{RNH_3^+} + \Gamma_{RNH_2}) d\mu_{RNH_2} - \Gamma_{Cl^-} d\mu_{HCl} \quad (75)$$

from which

$$\left(\frac{\partial \gamma}{\partial E_H} \right)_{\mu_{HCl}, \mu_{RNH_2}} = q_s \quad (76)$$

i.e. the familiar Lippmann equation.

Also

$$\left(\frac{\partial \gamma}{\partial \mu_{RNH_2}} \right)_{E_H, \mu_{HCl}} = - (\Gamma_{RNH_3^+} + \Gamma_{RNH_2}) \quad (77)$$

and

$$\left(\frac{\partial \gamma}{\partial \mu_{\text{HCl}}} \right)_{T, P, \mu_{\text{RNH}_2}} = - \Gamma_{\text{Cl}^-} \quad (78)$$

Rearrangement of (76), (77) and (78) gives two additional equations of interest

$$F(\Gamma_{\text{H}_3\text{O}^+} - \Gamma_{\text{RNH}_2}) = q_s - F(\Gamma_{\text{RNH}_3^+} + \Gamma_{\text{RNH}_2}) + F\Gamma_{\text{Cl}^-} \quad (79)$$

and

$$q_s = F(\Gamma_{\text{H}_3\text{O}^+} + \Gamma_{\text{RNH}_3^+}) = q_s + F\Gamma_{\text{Cl}^-} \quad (80)$$

where q_s is the charge due to the total surface excess of positive ions in the double layer.

If we use a calomel electrode instead of an hydrogen electrode equation (73) may be re-written

$$dE = dE_{\text{cal}} - \frac{1}{F} d\mu_{\text{Cl}^-} \quad (81)$$

and it may be easily shown that

$$\left(\frac{\partial \gamma}{\partial E_{\text{cal}}} \right)_{T, P, \mu_{\text{RNH}_2}} = q_s \quad (82)$$

Thus a complete thermodynamic analysis for the system $\text{RNH}_3^+ \rightleftharpoons \text{RNH}_2 + \text{H}^+$ is deduced. It is interesting to note from (77) that only the sum and not the individual values of $\Gamma_{\text{RNH}_3^+}$ and Γ_{RNH_2} can be determined. Moreover, the analysis can provide only the difference between $\Gamma_{\text{H}_3\text{O}^+}$ and Γ_{RNH_2}

[equation (79)]. With permanently quaternised salts, e.g. N-methyl-pyridinium chloride, however, the individual value of Γ for the organic cation can be unambiguously deduced as will be shown in a later section of the thesis.

F. ELECTROCAPILLARY STUDIES OF ADSORPTION OF NEUTRAL ORGANIC SPECIES

Gouy^{8,9,87-90} was the first to study the adsorption of neutral organic substances at the metal solution interface. It was found that these substances produced a truncation of the electrocapillary curve, i.e. the maximum lowering of surface tension occurred in the region of the e.c.m.

The first quantitative theoretical treatment was given by Frumkin^{91,92} who expressed the change in the work of adsorption resulting from the charge on the electrode as the sum of two terms:

(a) the first due to the smaller dielectric constant and greater length of the organic molecule than water. This term gives the change in the energy of the double layer "condenser" due to the change of its capacity as a result of the replacement of water by the organic substance, i.e.,

$$1/2 (C - C') (E - E^0_{C=C'})^2 \quad (83)$$

where C' is the capacity per square centimetre when the surface is saturated with the organic substance, C its capacity in the absence of any organic solute, E is the potential under

consideration, and $E^{e.c.m.}$ the potential of the e.c.m. for a given solution of the organic solute.

(b) An energy term dependent upon the dipole moment (through C') of the adsorbed molecule, i.e.,

$$C' (E - E^{e.c.m.}) (E_{\infty}^{e.c.m.} - E_0^{e.c.m.}) \quad (84)$$

where $E_0^{e.c.m.}$ is the potential of the e.c.m. in the absence of the organic substance and $E_{\infty}^{e.c.m.}$ is its value when the interface is saturated with the organic solute. Equation (84) gives the energy required to form a dipole layer at the electrode. Adding (83) and (84), and multiplying the total by S , the area of metal surface covered by one molecule of adsorbate, we obtain " W_e " the total electrical work of adsorption.

$$W_e = W_0 + S \left[-\frac{1}{2}(C-C')(E-E^{e.c.m.})^2 - C'(E-E^{e.c.m.})(E_{\infty}^{e.c.m.}-E_0^{e.c.m.}) \right] \quad (85)$$

The work of adsorption is thus related to the interfacial potential difference. In the absence of the electric field $W_e = W_0$. The effect of the change in the work of adsorption on the amount adsorbed is considered to be equivalent to a concentration change of $\exp (W_e/kT)$. The extent of surface coverage as a function of potential and of concentration is then obtained by using the Gibbs² equation, and an equation of state for the adsorbed film which allows for the attractive force between the molecules through a term analogous to the a/v^2 term in the Van der Waals equation. Electrocapillary curves for mercury in the presence of t-amyl alcohol were

derived by Frumkin's equations and found to be in excellent agreement with the experimentally determined curves obtained by Gouy for the same solutions. Frumkin's theory is somewhat empirical in nature because the constants required are calculated from the electrocapillary curves themselves. The treatment does not give an entirely satisfactory physical picture of the adsorption process.

A different but more satisfactory treatment of the effect of the double layer field on the adsorption of organic molecules has been given by Butler.⁹³ In Butler's theory the dependence of the amount of non-electrolyte adsorbed on the nature and concentration of the primitive electrolyte is not considered but this could easily be remedied by introducing a relation (i.e. an isotherm) between surface and solution solute activities through a standard electrochemical free energy of adsorption (see below). The theory has the advantage of giving a molecular picture of the adsorption process.

Butler considers the distribution of solvent and organic solute in the field of the electrode. A quantity of solute is assumed to be brought up to the double layer where the field is F and a corresponding volume of solvent is removed. The work done, per unit volume of the dielectric, against the electric forces in the transfer of a molecule of solute from the solvent is given by

$$W = 1/2 (\alpha_A - \alpha_B) F^2 \quad (86)$$

where W is the work, F the electrical field strength, and α_A and α_B are the polarizabilities of the solvent (A) and the solute (B) respectively. Equation (86) is then introduced into a Boltzmann distribution equation for the amount adsorbed, such that the surface excess Γ is related to the field by the following expression

$$\Gamma = \Gamma_0 \exp \left[1/2 (\alpha_B - \alpha_A) F^2 / kT \right] \quad (87)$$

where Γ_0 represents the surface excess when $F = 0$.

$\Delta\gamma$ and $\Delta\gamma^{\text{e.c.m.}}$, the depressions of surface tension when the fields due to excess charge at the surface are F and zero respectively, are assumed to be proportional to Γ and Γ_0 so that equation (87) becomes

$$\Delta\gamma = \Delta\gamma^{\text{e.c.m.}} \exp \left[1/2 (\alpha_B - \alpha_A) F^2 / kT \right] \quad (88)$$

If, in addition, the molecules possess permanent dipole moments then there will be another term to be included,^{94,95} and the expression becomes*

$$\Delta\gamma = \Delta\gamma^{\text{e.c.m.}} \exp \left[\frac{1}{2} (\alpha_B - \alpha_A) + (1/3 kT) (\mu_B^2 - \mu_A^2) \right] F^2 / kT \quad (89)$$

where the average effective dipole moment $\bar{\mu}$ is $\mu^2 F / 3kT$ (90)

Equation (89) reduces to

* Here we have modified the original treatment to show the result at both low and high fields.

$$\Delta\gamma = \Delta\gamma^{\text{e.c.m.}} \exp \left[\frac{1}{2}(\alpha_B - \alpha_A) F^2 + (\bar{\mu}_B - \bar{\mu}_A) F \right] / kT \quad (91)$$

when the double layer field is large/ ^{and} the average dipole moment $\bar{\mu} = \mu$, the actual dipole moment.

In Butler's treatment the field F is assumed to be proportional to the potential of the electrode E with respect to that of the e.c.m. In excess of neutral electrolyte, the potential difference in the double layer occurs mainly across the Helmholtz part so that this assumption is justified under certain experimental conditions. Equation (89) can hence be transformed into

$$\Delta\gamma = \Delta\gamma^{\text{e.c.m.}} \exp [-a(E - E^{\text{e.c.m.}})] \quad (92)$$

The term "a" in (92) is a constant involving α_A , α_B and the proportionality constant between E and F . Butler showed that the calculated values of "a" were in agreement with the experimental ones, although there were a few exceptions. For example, on the positive branch of the electrocapillary curve of o-cresol, the calculated lowering is greater than that observed experimentally. The agreement is better on the cathodic side of the e.c.m. The explanation of the discrepancy on the positive branch is simple. Butler's theory does not account for the dependence of the amount of non-electrolyte adsorbed on the nature and concentration of the primitive electrolyte. Generally, in experimental work, the concentration of the primitive electrolyte is usually quite high. Also, we

expect disagreement on the anodic side of the electrocapillary curves because it is in this region that anions are specifically adsorbed. Other problems, connected with the present writer's researches, arise in the study of adsorption of neutral organic molecules and will be discussed in detail in later sections of this thesis.

C. EXPERIMENTAL DETERMINATION OF ADSORPTION AT ELECTRODES

Methods available for the determination of adsorption at electrodes may be suitably divided into five categories: (i) electrocapillary studies; (ii) drop weight surface tension studies; (iii) surface tension studies at solid metals; (iv) the capacity method and (v) direct methods.

(i) Electrocapillary Studies

Historically, the electrocapillary method is the forerunner of all modern methods for the study of adsorption at electrodes. Although it dates back nearly ninety years, the method has been used frequently up to the present time. Moreover, it is often found that modern adsorption data obtained by other methods compare favourably with electrocapillary results. In this section we shall limit the meaning of the term electrocapillary studies to those measurements made in a capillary tube where that excess pressure is measured which is required to maintain the mercury meniscus at a fixed point

in a fine bore capillary.

The basis of electrocapillary studies lies in the discovery that when a mercury electrode is polarised, its surface tension changes (see page 47). Lippmann^{67,68,96} was the first to examine this effect quantitatively and he made use of it in the electrometer which bears his name. In most of the early methods for measuring potential differences, a Lippmann electrometer was used in place of a galvanometer as a current detector. The Lippmann electrode provides a convenient way of obtaining information about adsorption at its metal-solution interface. By application of the Gibbs⁹⁵ equation, the rate of change of surface tension with the chemical potential of one substance in the solution, the ^{of which} concentration/_{is varied} gives directly a measure of the amount of substance adsorbed.

Several workers⁹⁷⁻¹⁰¹ have made a series of small changes in both design and technique of operation of the capillary electrometer. For example Koenig found that if the mercury was kept at a position such that it was more than 0.1 cm from the end of the capillary the slight amount of hydrogen which was slowly liberated at the capillary electrode could not diffuse out fast enough, but would form bubbles of hydrogen inside.

Hansen and Williams were concerned with measuring the displacement of the s.c.m. of mercury for various solutions (1M, 0.2M, 0.02M aqueous ammonium nitrate) at 25° C, 50° C and 75° C. Their essential modification lies in the attachment of a side arm joined to a reflux condenser. Because temperatures from 25° C to 75° C were used, it was necessary to employ the reflux condenser to keep the pressure in the cell equal to the atmospheric pressure without changing the composition of the solution. Crawford and Devanathan paid special attention to the purity of solutions. Their results indicate that there is little difference between the older results of Gouy⁸⁷⁻⁹⁰ and the newer results.

The most thorough investigation of the dependence of the electrocapillary curve on the composition was made by Gouy who used aqueous solutions of many organic and inorganic compounds, and a few non-aqueous solutions. He demonstrated that there are several electrolytes which appear to have no specific effect on the electrocapillary curve; the results for these solutions being almost identical. For example, the magnitude of the surface tension at the s.c.m. (γ_{max}) was found to be equal within ± 0.2 percent for distilled water, N KOH, N NaOH, 0.01N KNO₃, N K₂CO₃, 0.1M K₂HPO₄, 0.1M KH₂PO₄, 0.1M KAsO₄, 1M H₃PO₄, N Na₂SO₄, N Mg₂SO₄, 0.17N Al₂(SO₄)₃ and N H₂SO₄. The comparative

insensitivity of γ^{max} to the composition of the solution is quite remarkable because it shows that γ^{max} is not affected either by hydrogen or hydroxyl ions, or by the valency of the heavier ions. γ^{max} for $\text{Hg}/\text{H}_2\text{O}$ at 18°C was found by Gouy to be 426.7 dynes/cm. whereas in $\text{N H}_2\text{SO}_4$ γ^{max} becomes 426.3 dynes/cm.

Gouy did, however, discover that many other electrolytes gave very different values of γ^{max} . He also found that the value of γ^{max} is raised by relatively few salts and then only to a relatively small degree. The highest γ^{max} value recorded by Gouy is 6.6 percent above that of water, and was observed in 7.74 N solution of K_2HPO_4 . This result would appear to be thermodynamically possible only if negative adsorption of the solute salt occurred (as it does at the air-water interface in certain systems). A reduction in γ^{max} was encountered more often, e.g. 2 moles per litre of KCN reduced γ^{max} by 5.5 percent, 0.5 moles per litre of $\text{K}_2\text{Pt}(\text{CN})_4$ by 6.7 percent, 1 mole per litre of potassium iodide by 6 percent, and so on.

Electrolytes which affect γ^{max} also influence the potential at the e.o.m. ($\phi^{\text{e.o.m.}}$). The following table illustrates some of the results obtained by Gouy

Table I

Solution	H ₂ SO ₄	HNO ₃	HCl	KBr	KI	0.5M K ₂ Pt(CN) ₄	0.17M Al ₂ (SO ₄) ₃
$\phi^{e.c.m.}$ in volts	0.48	0.56	0.56	0.65	0.82	0.76	0.48

Potentials of mercury at the e.c.m. are measured against a normal calomel electrode

Inspection of the above table shows that $\phi^{e.c.m.}$ is influenced more by anions than cations, a result related to the stronger specific adsorption of anions than of cations.

Another noticeable effect is that the width of the electrocapillary curve is affected both by the nature and the concentration of the aqueous phase. The width is the difference of the potentials corresponding to one value of γ on the two branches of the curve. From Hansen and Williams⁹⁹ data, it can be shown that in 0.2 M NH₄NO₃ solution at 25° C an interfacial tension of 392 dynes per centimetre is observed at 0.456 and 1.446 volt. Hence the width of the curve at the level of 392 dynes per centimetre is 0.990 v. The following table show (Table II page 74) some other examples taken from Gouy's results. The variation of width at a given γ for various salts again reflects specific adsorption effect on one branch or the other.

Table II

Interfacial tension γ dyne/cm.	$\gamma^{\max} - \gamma$		Width (volts)	
	N KNO_3	0.1 N KI	N KNO_3	0.1 N KI
461	26	14	0.767	0.444
384	43	31	1.059	0.682
367	60	48	1.296	0.861
350	77	65	1.497	1.009

Rein and Markov²⁷ examined the electrocapillary curves for aqueous solutions of potassium iodide and related the o.c.m. potentials to the electrolyte concentration; the shift of o.c.m. potential with concentration is important in the theory of the double layer and this effect has been named after them. Frumkin and Jofa¹⁰² presented electrocapillary curves for concentrated solutions of acids. They emphasized the need for the use of an auxiliary electrode reversible to one of the ions in solution, for example the hydrogen electrode or a calomel electrode in the case of hydrochloric acid solutions. Frumkin and Jofa obtained very precise values of $\beta^{\max}$ (with respect to an hydrogen electrode) and $\gamma^{\max}$ for hydrochloric acid at various concentrations;

typical data are shown below (Table III) since these results form the basis for calibrating solutions used in the present and other recent work.

Table III

Normality	0.1	1.0	2.0	3.0	5.0	7.0	9.0	10.0
ϕ_{max} (volts)	-0.185	-0.293	-0.355	-0.407	-0.495	-0.595	-0.670	-0.710
γ_{max} (dynes/cm)	425.7	423.0	420.7	418.1	414.6	412	408.7	409.3

Butler¹⁰³ examined the lowering of surface tension produced by iodides. He showed that anions caused a considerable lowering on the extreme left (the positive branch) of the electrocapillary curve, in contrast to a negligible effect on the negative branch. He demonstrated that the lowering in surface tension due to iodides could be expressed as follows:

$$\log (\Delta \gamma) = \text{Constant} - \alpha eV/kT \quad (93)$$

where αeV is the work done by an ion of charge 'e' as it became adsorbed by passing through a fraction α of the total metal-solution potential difference to some equilibrium position in the double layer at the electrode interface.

Generally, inorganic cations show no marked specific adsorbability at the Hg-solution interface. Franklin¹⁰⁴ and

his co-workers^{105,106} have recently shown that thallous ions are adsorbed in a manner which is quite comparable with that for inorganic anions. Parsons and Anderson¹⁰⁷ determined the effect of temperature on the electrocapillary curve of mercury against aqueous potassium iodide solutions. The isotensile or "equilibrium" heats of adsorption and the corresponding entropies were calculated from their data. Their results are stated to be only preliminary in nature and require confirmation by measurements of the properties of other specifically adsorbed ions, and also by measurements of differential capacities.

Devanathan and Peries³⁰ made electrocapillary measurements for mercury in aqueous potassium halide solutions using a reference electrode in the same solution. A calomel electrode was used for experiments with potassium chloride solutions and a mercury/mercurous bromide electrode was used for potassium bromide solutions. For potassium iodide solutions, a silver/silver iodide electrode was employed. The cell used by these workers was relatively simple, but it contained a few novel features hitherto unused by others. It consisted of a three necked glass tube with a gas inlet and outlet. Through the centre of the tube was located the mercury electrode. The auxiliary electrode (platinised platinum) and the reference electrode were inserted in the two other necks of the tube. Their results permitted the exact calculation of ionic components of charge for the above electrolyte solutions at the

mercury-solution interface; the computed values agreed well with those evaluated from differential capacity measurements.

Brief mention must be made of some electrocapillary work done in non-aqueous solvents. Franklin¹⁰⁸ in 1923 reported data for NH_4NO_3 , NaBr and NaI in methanol, NH_4NO_3 , LiCl and NaI in ethanol, LiCl in a mixture of ethanol and water, LiNO_3 , LiCl and NH_4CNS in acetone, and NH_4CNS and NaI in pyridine. Parsons and Devanathan¹⁰⁹ described measurements of the electrocapillary curve for solutions of hydrogen chloride in methanol-water mixtures. The effect of acid concentration on the rate of hydrogen evolution from aqueous and methanolic solutions would be interpreted in terms of the electrocapillary results and the calculated behaviour was shown to be consistent with that observed experimentally. In 1931, Ockrent¹¹⁰ investigated the electrocapillary behaviour of mercury in various alcohol-water mixtures, but the results presented by this worker have no clear thermodynamic significance. Firstly, the potential of the capillary electrometer in contact with a solution in a given mixed solvent was measured with respect to an aqueous normal calomel electrode. This introduces a liquid junction potential of unknown magnitude into each measured potential. Secondly, a single high concentration of electrolyte was used, so that the surface excess of solute could not be calculated, and although in the mixtures varying chemical potentials of alcohol and water were

examined, no relative values of γ_{H_2O} and γ_{ROH} were calculated.

Measurements of the electrocapillary curves for amalgams were made by Gouy.⁹⁰ He used 0.1 percent amalgams of Sn, Pb, Cd, Bi and Zn. Frumkin and Gorodetskaja¹¹¹ recorded electrocapillary curves for thallium amalgams (up to 41.5 percent thallium) at potentials for which the anodic dissolution of thallium was negligible, so that the concentration of the amalgam remained constant. In normal sodium sulphate solution, thallium lowers the mercury-solution interfacial tension if the potential is larger than -0.75 volt, and raises γ for more negative potentials, so that the electrocapillary curve for the amalgam cuts that of mercury in the neighbourhood of this potential. The maximum of the electrocapillary curve is displaced by thallium in the direction of more negative potentials.

A smaller, simpler and consequently less accurate form of capillary electrometer has been used for measurements at higher temperatures. The electrocapillary curve for molten gallium (M.P. 29.8° C) in salt solutions was studied also by Frumkin^{and} Gorodetskaja¹¹¹ and the electrocapillary curves of molten metals in molten electrolytes were obtained by Karpatchev et al.¹¹²⁻¹¹⁸ who used in most of their work the potassium chloride-lithium chloride eutectic as electrolyte

and electrodes of pure antimony, tin, cadmium, lead, zinc, thallium, silver, bismuth, aluminium, gallium, tellurium, and thallium, tin and bismuth amalgams, as well as tin-zinc, tin-antimony and bismuth-tellurium alloys. Bismuth had a γ^{max} value of 376 dynes per centimetre in the eutectic mixture of potassium chloride and lithium chloride at 450° C, and $\phi^{\text{e.c.m.}}$ was -0.3 volt referred to a lead electrode in the same melt. It may be noted that it is difficult, if not impossible, to correlate data of this kind with those obtained on mercury in contact with aqueous solutions at low temperatures.

In the earlier work, electrocapillary studies of organic molecules and ions appears to be somewhat unsystematic. Thus Gouy (loc. cit) showed that amyl alcohol had very little effect on the interfacial tension of mercury in a primitive normal solution of sodium sulphate at potentials far from the e.c.m. but found however, that depression of the surface tension of mercury occurred near the e.c.m. and made the curve very asymmetric, so much so that the e.c.m. is shifted by about 0.3 volt. Many other organic compounds shifted $\phi^{\text{e.c.m.}}$ towards higher cathodic potentials (i.e. in the direction opposite to that for amyl alcohol). The substances used by Gouy included resorcinol, phenol, pyrogalllic acid and biuret.

Butler⁹³ examined the electrocapillary behavior at mercury of acetic, propionic and monochloroacetic acids.

He also studied pyrrole, triethylamine and isobutylamine. By consideration of these data, he evolved the theoretical considerations discussed in the earlier part of this review (q.v. Chapter I, section F, Page 66). Individual capillary curves for solutions of tetra-alkyl ammonium ions have been given by Frumkin.⁶⁹ More recently, Conway, Bockris and Lovrocek⁶³ determined the adsorption of certain alkaloids from electrocapillary measurements in order to interpret some anomalous kinetic effects at mercury. Bockris and Blomgren,³¹ and Antropov and Banerjee^{83,85} have studied the adsorption of organic compounds at the mercury-aqueous acid solution interface in relation to corrosion inhibition. Gierst and his coworkers⁸⁶ have examined the adsorption of amines from neutral solutions.

Generally, the electrocapillary data in the older literature (prior to about 1940) for inorganic and organic compounds are of little value for quantitative interpretation in terms of the modern aspects of electrified metal-solution interface theory. Many of the older workers used only single concentrations of additives, and others made no effort to correct for liquid junction potentials. The situation for inorganic additives is considerably better than for organic additives. There is undoubtedly a very distinct scarcity of thermodynamically significant data in the studies of adsorption of organic substances at metal-solution interfaces, and a corresponding lack of knowledge of the structure of the

double layer either for neutral or ionic organic species.

(11) Drop-Weight Studies

A rapid method for obtaining a measure of surface tension is the "drop weight" or "drop volume" method. Using a polarograph¹²⁰ drop times (which are inversely proportional to the corresponding drop weights) can be plotted against the potential of the mercury drops and a curve is obtained which is almost identical with an electrocapillary curve. The same experimental arrangement is used as in the ordinary polarographic determination of current-voltage curves.

Kucera¹²¹ was the first to employ the drop weight method but there has been much controversy concerning whether satisfactory electrocapillary curves can be obtained by this method. There is no satisfactory theoretical relationship between the drop weight and the interfacial tension; they appear to be proportional to one another and the proportionality constant can be evaluated empirically. Crazford and McKay¹²² developed two forms of apparatus which they used for the determination of the drop weight "electrocapillary" curves under air-free conditions. They obtained values of the interfacial tension of mercury at various applied potentials in a normal solution of potassium nitrate, which were identical (to within 0.2 percent) with those obtained by means of a capillary electrometer. Though apparently simple, the drop weight method is experimentally tedious and difficult to operate

because of the necessity of counting the drops and also because the electrolyte tends to creep up the capillary causing irregular drop formation and erratic results.

(iii) Surface Tension - Potential Curves for Solid Metals

An interesting method of measuring the surface tension between a solid metal and a solution, first developed by Moeller^{123,124} has been applied by Frumkin¹²⁵ and his colleagues.^{126,127} The contact angle β of a bubble is related to the tensions of the three interfaces, namely, $\gamma_{g/l}$ (gas/liquid), $\gamma_{g/s}$ (gas/solid) and $\gamma_{l/s}$ (liquid/solid), by the following equation

$$\cos \beta = \frac{\gamma_{g/s} - \gamma_{l/s}}{\gamma_{g/l}} \quad (94)$$

and only $\gamma_{l/s}$ is regarded as varying with potential. Curves similar to those obtained by the electrocapillary method using mercury are obtained by plotting the contact angle against the potential of the metal. With mercury, $\gamma^{c.e.m.}$ is in the same region as that previously found with a capillary electrometer. Values of $\gamma^{c.e.m.}$ for copper, nickel, silver, platinum, zinc, gallium and amalgams of thallium were determined. The contact angle method is not as accurate as the electrocapillary method. The irreproducibility may be due to unsatisfactory cleaning of the solution and of the metal surface. It is of interest to note that Frumkin and Gorodetzka¹²⁸ claimed

that if the bubble size were plotted against the electrode potential, a curve similar to the electrocapillary curve was again obtained.

Rehbinder and Wenstrom¹²⁹ devised a novel apparatus for measuring the effect of polarisation on abrasion resistance. Essentially it consists of a heavy pendulum which rubs against the solid whose abrasion resistance is determined. In the course of the pendulum's oscillation the pivot of the pendulum rubs against the solid, and the decay of the oscillations is more rapid the lower the abrasion resistance of the solid. The abrasion (sometimes also referred to as the hardness) takes place in a drop of liquid put on the surface of the solid. The solid is connected to one pole of the potentiometer, and the other terminal of the potentiometer is connected to a platinum wire immersed in the drop of liquid. A glass bead at the end of the platinum wire prevents contact between the platinum and either the pendulum base or the solid. When the potential difference between the platinum and solid varies, a plot of abrasion resistance versus potential gives curves similar to an electrocapillary one. Comparative experiments of abrasion resistance and interfacial tension of thallium and thallium amalgams with solutions of sodium sulphate, and sodium sulphate and amyl alcohol were reported by Frumkin.¹³⁹

The existence of a relation between surface tension of the metal-electrolyte system and the hardness of the metal

surface as measured by the logarithmic decrement of the oscillations of the pendulum has been confirmed by Eockris and Parry Jones.¹³¹ They repeated the work of Wenstrom and Rehbinder and showed that $\beta^{0.6.20}$ for amalgamated copper is identical with that obtained from electrocapillary curves of mercury in the same solution. However, they claim that the property measured is not the hardness of the metal; it is probably related to the friction between the pendulum and the solid metal plate.

(iv) The Capacity Method

It has been mentioned in an earlier section of this review (q.v. page 60) that the capacity of the electrode-solution interface may be obtained from the slope of the charge-potential plot, or by differentiating the electrocapillary curve twice:

$$C = \partial q_x / \partial E = - \partial^2 \gamma / \partial E^2 \quad (95)$$

The electrode capacity may, however, also be obtained by direct experiment. Basically, the impedance of the metal-solution interface is required. The ohmic resistance of the solution can be regarded as being in series with the impedance of the interface, and can be vectorially subtracted out of the total measured impedance. Various techniques for measuring electrode capacities have been reviewed in the recent literature,^{32,132} and Parsons²⁵ in particular, has concisely summarised the more important contributions made by workers

in the Soviet Union. The most significant Western worker in this field has been the late D.C. Grahame¹³³⁻¹⁴⁰ who measured the capacity of the mercury electrode in a variety of solutions by means of an a.c. impedance bridge.

Essentially Grahame's apparatus consists of a dropping mercury electrode issuing from the tip of a thin-walled capillary. The droplet of mercury is surrounded with a deaerated solution of an inert electrolyte (say potassium chloride) and the capacity is measured. The bridge is balanced at one moment only during the life of a drop, and the age of the drop at this moment must be accurately measured with a stop watch or preferably an electronic timer. It may be pertinent to point out that Grahame's technique for measuring the differential capacity of the electrical double layer is based on the first successful application of this type of measurement by Proskurnin and Franklin.¹⁴¹ It is necessary for success in these measurements to produce a clear smooth surface with all the elements of the surface exposed to the same conditions of current flow.¹³⁹ The use of mercury is an effective way of satisfying these requirements. Minor modifications to the bridge impedance method have been reported by a number of other workers.¹⁴⁰⁻¹⁴⁵

The capacity method would appear in principle to be the most useful one for studying the double layer at solid

metals. However, few studies of this type have been reported in the literature. Grahame³² has reviewed the existing capacity results for platinum but the data of various investigators are, however, discrepant. This may possibly be due to the lack of uniformity in electrode surface preparation.¹⁴⁶ Capacity data at solid metals are very much dependent on frequency^{19,52,147,148} and Bockris and Conway¹⁴⁹ have shown that the variation of the double layer capacity and resistance at metals is intrinsically frequency dependent. They explained the variation of the double layer capacity with frequency as being due to dielectric loss in the layer of adsorbed water molecules in the interphase.

When the surface of the electrode is covered with adsorbate, it is found that there is a variation of the capacity with frequency and a complementary way of stating Bockris and Conway's explanation is that the variation is due to the oscillations of the metal-adsorbate dipoles in the a.c. field. Furthermore, it is noted that fresh surfaces of electrodes prepared by cutting the surface shows a high variation of capacity with frequency, and this may be reduced by melting the surface of the electrode to remove irregularities.¹⁴⁶ The variation with frequency at an irregular surface is also due to the fact that the electrode and solution may not behave as a simple capacity and resistance in series because

of the non-uniform distribution of current over the electrode. For obvious reasons, mercury shows the least frequency dependence of capacity.

Recently Schagink et al.¹⁵⁰ have studied the adsorption of thiourea, aniline and mixtures of the two in aqueous and methanolic solutions of 0.1 molar sodium fluoride using Grahame's a.c. impedance bridge technique. Generally, Grahame's method gives accurate measurements of the capacity within one percent, but this type of accuracy is not applicable to electrodes which exhibit large capacities.

Roughness factors, that is the ratios of true to apparent surface areas of solid electrodes, have been determined by capacity measurements.¹⁵¹ In this way it is found that "smooth" common metals have true areas which are up to approximately three or four times greater than their apparent areas. An assumption that for mercury $C_{\text{apparent}}/C_{\text{true}} = 1$ is reasonable, and probably correct. The differential capacity measurements for mercury can be checked by electrocapillary methods, but data for solid electrodes cannot be checked so readily. In this connection, it is encouraging to note that Hackerman and his collaborators^{152,153} have reported good correlation for solid electrodes between areas calculated from capacity data and those measured by means of krypton adsorption. Their capacity data were obtained from time/potential traces

observed when a square wave signal was applied to the electrodes. Their method was based on that suggested by Bowden and Rideal¹⁵⁴ who obtained capacities by direct charging, on the assumption that any current supplied to the electrode was involved in charging the electrical double layer, i.e. the interface was an ideally polarisable one.

Hansen and Claspitt⁵⁷ derived apparent isotherms for the adsorption of organic compounds such as, n-caproic acid, n-heptaldehyde, n-octanoic acid, n-heptylic acid, acetic acid and heptanol-1, on silver and copper electrodes by means of double layer capacitance and steady state current-overvoltage techniques. The double layer capacitance was used to infer the extent of the adsorption of the surface active organic compounds on the solid metals. The measured capacitance was assumed to be proportional to the area of surface free^{of} adsorbate so that the surface coverage was obtained as

$$\theta = 1 - \frac{C}{C_{\theta=0}} \quad (96)$$

Apparent fractional surface coverages found by capacitance measurements were compared with those obtained by steady state current-overvoltage measurements at two currents. The results were stated to be in reasonably good agreement.

Hansen, Minturn and Hickson¹⁴³ re-investigated the method originally developed by Frumkin⁹¹ and Barclay and

Butler:¹⁵⁵ The surface coverage in Frumkin's treatment was expressed by Hansen and his coworkers in terms of the differential capacity of the double layer in order to relate experimentally the surface coverage to the concentration and potential. Butler and Barclay included a brief study of the effect of t-amyl alcohol on the double layer capacitance at the mercury surface but they did not attempt quantitatively to correlate the effects observed with adsorption, nor did they investigate the dependence of these effects on polarisation. Hansen et al. gave a relationship between the differential capacitance, the electrode polarisation, and the fraction of surface covered in a monolayer process. A detailed study was made by these workers to verify the predicted relationship.

Hansen and his co-workers found a simple Langmuir adsorption isotherm to express the differential double layer capacity (or the fraction of surface covered) as a function of the concentration in solution.

$$\theta = \frac{C_{d.l.}^0 - C_{d.l.}}{C_{d.l.}^0 - C_{d.l.sat.}} \quad (97)$$

At the potential corresponding to maximum adsorption, where the variation of adsorption with electrode polarisation can be neglected, the fraction θ of surface covered was related to the differential capacity per unit area $C_{d.l.}$ by the above equation. $C_{d.l.}^0$ is the value of $C_{d.l.}$ in the absence of

surface active agent, and $C_{d.l.sat.}$ is the value corresponding to a saturated monolayer. At other potentials, θ can be replaced by $\theta_{apparent}$ the apparent fraction covered. The value of $C_{d.l.sat.}$ can, in principle, be determined by measuring the complete adsorption isotherm. It may be noticed that equation (97) is the quantity measured by Hansen and Claspitt (loc. cit) where $C_{d.l.}$ was neglected. Laitinen and Kosier¹⁵⁶ extended the application of the work of Hansen and his coworkers to other systems.

The a.c. resistance of a stainless steel wire electrode was measured by Schmid and Hackerman¹¹⁹ as a function of the type of electrolyte, the polarising current density and frequency of the measuring current. The method depends on the behaviour of the electrode and electrolyte solution comparative to an analogue of two resistors connected in parallel. When potential is applied to the electrode in solution, a certain fraction of the total current flow passes through the electrical double layer and the solution. The extent of this leakage was found by measuring the impedance of the system and comparing with the impedance of the electrode in air. The difference between impedance measurements with low frequency a.c. in air and in solution was small but when the electrode is sufficiently polarised to make an electrochemical reaction possible the capacity became appreciably higher and/or the resistance dropped to low values. This

causes an a.c. leakage as evidenced from graphical plots of potential and current density versus impedance. The better conducting electrolyte, potassium sulphate, showed a lower impedance at a given potential and current density than sodium sulphate. The distance between anodic and cathodic curves is slightly larger in the case of potassium sulphate thus pointing to a more densely packed double layer. From this, the conclusion was drawn that during cathodic polarisation, K^+ ions were more adsorbed than Na^+ ions. Potassium halide salts were also examined and the results indicated, e.g. that during anodic polarisation Cl^- ions were more adsorbed than F^- ions. In common with capacity methods discussed in this section, this method is also limited by a dependence of impedance on frequency.

(v) The Direct Determination of Adsorption at Electrodes

Despite the general importance of the problem of evaluation of adsorption of electrolytes and organic compounds at electrodes, very little work has been reported on direct determination of adsorption by measurements of the change of concentration of a solution consequent on the introduction of a metal which adsorbs some constituent of the solution. The difficulty is in the limited range of concentrations which can be usefully studied. There is also a shortage of reliable and suitable chemical procedures available for detecting changes on an

ultra-micro analytical scale.

The use of radioactively tagged compounds offers interesting possibilities in this field and this has been developed for the adsorption of silver sulphate on silver using ^{35}S as tracer¹⁵⁷ and also for chromate and sulphate ions at iron surfaces.¹⁵⁸ This method is novel and interesting, but its value is somewhat diminished by the necessity for removal of the metal from the solution and subsequent washing of the metal. In certain systems, this procedure could displace the true thermodynamic equilibrium which had existed during the process of adsorption prior to removal of the metal, but the method is a valuable one when the adsorption is irreversible. The effect of potential on adsorption at these metals was not studied, but it would appear that the effect of polarisation could in some cases make the above mentioned disadvantage more pronounced.

The use of conductance measurements to follow the adsorption of ionic species from solutions at low concentrations as originally reported in the Russian literature, but without experimental details, is a promising technique although it would exclude the possibility of investigating the adsorption of neutral molecules. Changes in refractive index of binary liquid mixtures on adsorption of one component of the mixture by charcoal have been reported by Bartell and Sloan,¹⁵⁹ and by Kipling.¹⁶⁰ The measurements can be made with a Pulfrich refractometer or by means of a Rayleigh interferometer.¹⁶¹

This refractometric technique could conceivably be adopted for studying the adsorption of certain neutral organic molecules on metals, but it is obviously of limited application.

As a conclusion to this chapter a brief summary of the principal methods available for studying electrochemical adsorption and the salient features of their applications and limitations will be given in Table IV (page 94).

Table IV

Method	System where applicable	Principal limitations	Principal types of information or quantities obtained
1) Electrocapillary	Liquid metals, amalgams and molten metals	None except restriction to liquid metal phase	$\Gamma_A, \Gamma_+, \Gamma_-, q_M, q_s, \Delta \bar{G}^0$
2) Capacity (Grahame)	Solid and liquid metals	a) Requires at least one electrocapillary determination b) Frequency dependence of capacity	$\Theta, \Gamma_A, \Gamma_+, \Gamma_-, q_M, q_s, \Delta \bar{G}^0, C$
3) Capacity (Hansen)	Solid and liquid metal	a) Frequency dependence of capacity b) Thermodynamic interpretation not rigorous	Essentially similar to (2)
4) Radio isotopes	Solid electrodes	a) Irreversible adsorption or desorption b) Case where back count (C_{11}) can be done; significance of count may be in doubt	Θ , non-equilibrium values of in case (a) or equilibrium in case (b)

Table IV - (continued)

Method	System where applicable	Principal limitations	Principal types of information or quantities obtained
5) Spectrophotometric	Solid electrodes	a) Conjugated organic molecules b) Restricted application to certain organic ions and adsorbents	ϵ , Γ , $\Delta\epsilon^\circ$
6) Conductance	Solid and liquid electrodes	a) Ionic species but not neutral molecules	Speculative and not fully explored
7) Refractometric	Solid and liquid electrodes	a) Ionic and neutral molecules where changes in refractive index of adsorbate solutions are significant	Speculative and unexplored
8) a.c. Resistance	Solid electrodes	a) Frequency dependence of impedance measurements b) Uncertainty of equilibrium thermodynamic significance	Quantitative adsorption parameters not published.

CHAPTER II

PART I: ADSORPTION OF HETEROCYCLIC AND AROMATIC BASES

A. EXPERIMENTAL

(1) Introductory Remarks

Heterocyclic and aromatic nitrogen compounds in neutral or ionic form have been widely used as corrosion inhibitors^{162,163} or electrochemical additives¹⁶⁴ to modify the kinetics of various electrode processes. However, few data are available from which an elucidation of the factors determining the adsorption of simple organic bases at electrodes can be made (q.v. Chapter I) and systematic studies of the effects of ionisation by comparison between the adsorption of neutral bases and their corresponding quaternary ions have not been made. Of greater importance in relation to kinetic effects is ^{the structure} of the double layer in the presence of organic ions and neutral molecules and this has hitherto received little attention.

Previous work on neutral pyridine derivatives has been reported at mercury⁸⁶ but adsorption energies and isotherms have not been evaluated. Banerjee and Antropov^{83,84} have studied the adsorption of heterocyclic and aromatic aminium ions in sulphuric acid solutions at mercury and related their corrosion inhibitory power at iron to the depression of surface tension arising from adsorption of these compounds. More recently, during the course of the present work, Eockris and

Almgren¹¹ have related the surface coverage at the e.c.m. at mercury to the corrosion inhibiting power by similar cyclic organic bases and have studied the isotherms for the adsorption of some aniline ions in hydrochloric acid solutions.

In the present work, the aims have been (a) to investigate the relationship between adsorption and molecular structure of the heterocyclic and aromatic additives; (b) to evaluate the standard free energies of adsorption of these bases as a function of electrode potential and surface coverage and to examine the nature of the isotherm; (c) to compare the standard free energies of adsorption of the neutral bases with those of the corresponding ions formed by reaction of the base with an aqueous acid solution; (d) to investigate the role of π -orbital interaction with the electrode surface in determining the extent and free energy of adsorption; (e) to examine the structure of the electrical double layer by obtaining the ionic components of charge as a function of electrode potential; (f) to evaluate the extent of the Hain and Markov effect for specifically adsorbed organic cations and (g) to investigate an analogous "Hain and Markov effect" for neutral molecular species.

Throughout the work described in this chapter the mercury electrode has been used as in previous studies^{63,30} on account of the precision of adsorption data obtainable by means of surface tension measurements and since the electrode is almost ideally polarisable (loc. cit.). Also, use of the mercury electrode enables the adsorption data to be employed

directly in interpretation of related kinetic data which can be obtained with the best precision^{53,49} at this metal. A further advantage of mercury over solid metal electrodes (cf. Chapter IV) is that a wide range of electrode-solution potential differences can be examined without dissolution of the metal or electro-catalytic reduction of the additive.

(ii) Method

Adsorption of the organic additives was studied by determination of the surface tension of mercury using a capillary electrometer (vide infra). As discussed previously in Chapter I, Sections D (ii) and (iii), and C (i), electro-capillary curves may be derived. By applying the Gibbs adsorption equation to surface tension measurements as a function of electrode potential E and solute activity a_2 , the surface excess of additive as a function of electrode potential and solute concentration can be evaluated from the following equation

$$-\Gamma_2 = \left(\frac{\partial \gamma}{RT \partial \ln a_2} \right)_E, \left(\frac{\mu_{KCl}}{\mu_{HCl}} \right) \quad (98)$$

Adsorption isotherms can hence be obtained, and standard free energies of adsorption evaluated. The evaluation of other quantities will be discussed later.

(iii) Surface Tension Measurements

Despite the use of the capillary electrometer by various workers from 1875 to the present time, very few

details of its operation or of the optimum conditions required for obtaining results of the best precision have been published in previous papers. Accordingly, the following essential experimental technique and description of the electrometer is described below.

The two photographs (Figures IV and V on pages 100 and 101, respectively) show a close-up picture of the electrometer and of the electrometer with its full attendant assembly, respectively. For additional convenience and clarity, a schematic diagram of the essential parts of the apparatus is shown on Figure VI (page 102).

An all-glass cell, having three compartments, of the type employed in electrokinetic work was used.⁴⁹ The cell was designed to hold a rough vacuum without the use of greased joints by using carefully ground glass joints and taps which were sealed with the solvent which is used inside the cell. Such an arrangement permits the apparatus to be used with "deoxygenated" solutions. This is not a vital consideration since it has been stated by several modern workers^{30,165a} that the presence of oxygen does not vitiate the electrocapillary measurements, a fact which has been confirmed by the present writer. The important factor, however, is the exclusion of contamination by grease.

Provision was made in the large central compartment (see page 101) for immersion of a calomel electrode contained in a 12 mm. tube. Access of solution to the $\text{Hg}/\text{Hg}_2\text{Cl}_2$

Figure IV: Photograph of three compartment
capillary electrometer cell used
in the present work.

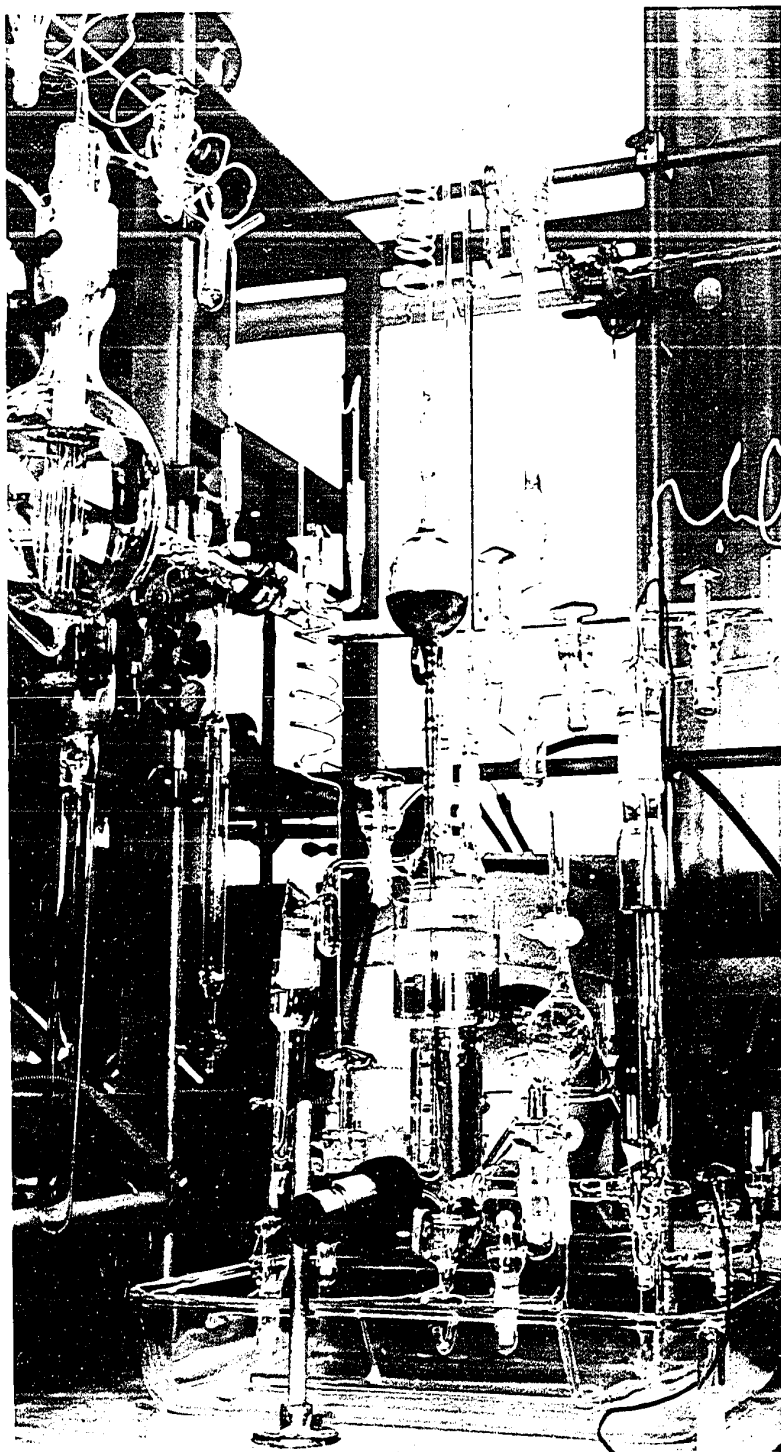
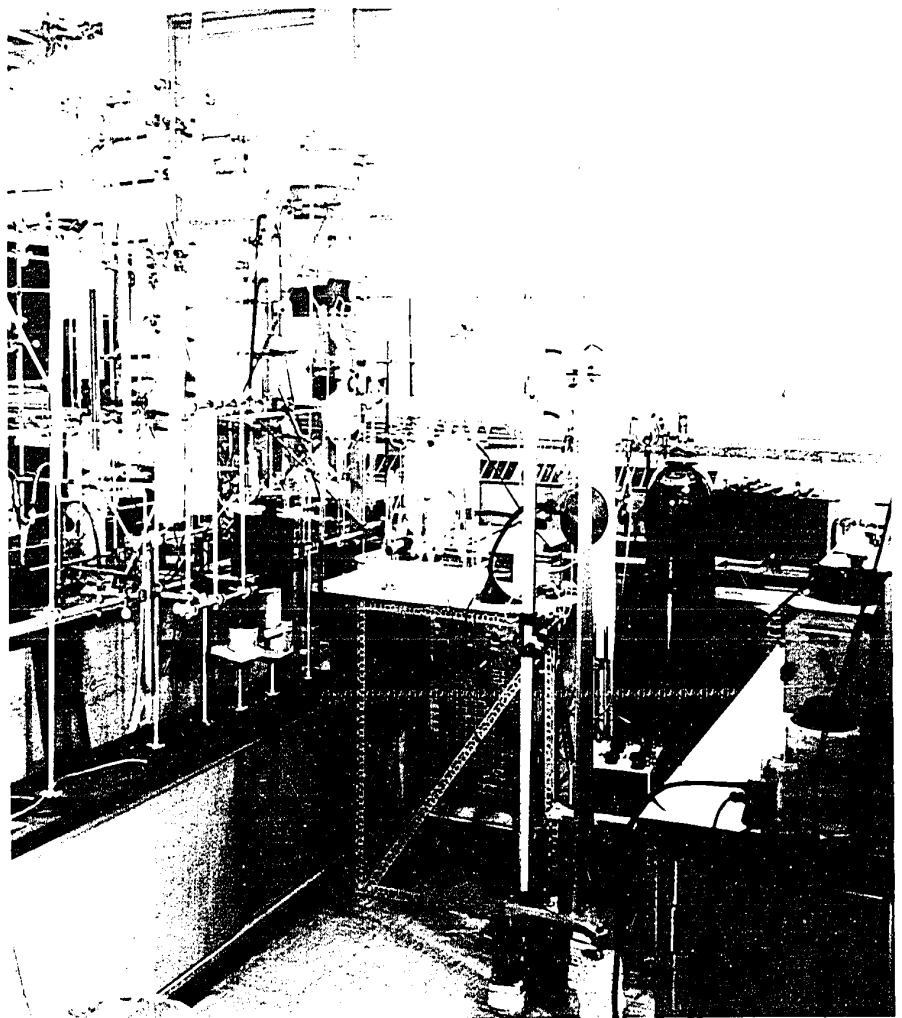
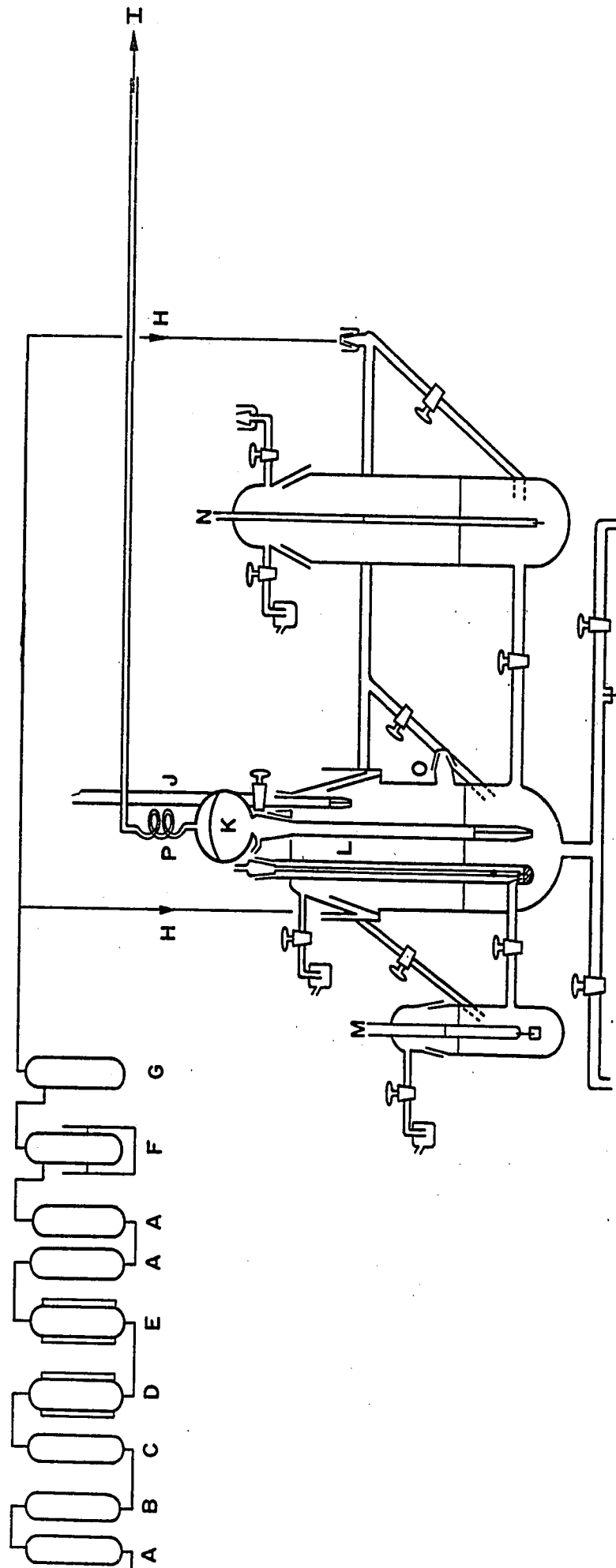


Figure V: Photograph of entire assembly of
apparatus used in the determination
of adsorption at mercury.



**Figure VI: Schematic diagram of the capillary
electrometer and its supplementary
apparatus.**



Schematic diagram of capillary electrometer: (A to G) gas purification train: A, Calcium chloride-magnesium perchlorate; B, Sodamine; C, Hopcalite; D, Copper turnings 450°C; E, Palladized asbestos; F, 3 activated charcoal traps in liquid air; G; Dust trap; H, Inlets to cell; I, Manometer, N₂ supply and regulators; J, Burette; K, Hg cathode; L, calomel electrode; M, H₂ electrode; N, Pt anode; O, Sample withdrawal outlet/thermo-meter; P, Detachable spiral glass coil.

interface was through two 1 mm. holes above the surface of the calomel. The calomel electrode was arranged in the cell to be as near as possible (3 mm.) to the mercury capillary in order to minimise ohmic errors at highest electrode potentials; these errors were in fact negligible. The left hand side compartment shown in Figure VI was provided to contain an hydrogen reference electrode, which in fact was not used for reasons to be discussed below. Such a reference electrode can be used as an anode as well. Since the area of this electrode is very much larger than that of the mercury in the capillary, the former is unlikely to be polarised, but the ohmic drop in the solution is included in the measured e.m.f. so that it appears preferable to have separate electrodes to perform the functions of anode and reference electrode. The platinum wire anode used was housed in the third compartment of the cell, and shown on the right hand side of Figure VI.

The mercury capillary was constructed from a 0.3 mm. pyrex capillary tube that had been previously cleaned in a nitric and sulphuric acid mixture, washed many times with conductivity water and then dried in an air oven. The capillary was then drawn down in a gentle taper over the last half inch of its length and finally the end was drawn again to a very small diameter in a small cool flame. Production of the capillary is critical, and a good one must have a very gentle taper over the last 5 mm. of its length and have a

sufficiently small diameter at its lower end to be able to support an open column of mercury about 8 inches high. It is important that the end be cut with a sharp tungsten carbide glass knife in order to avoid microscopic jaggedness, and consequent uneven break-away of the mercury drop as the meniscus is brought to a point near the end of the capillary.

The capillary was mounted at one end of a small male ground glass joint (10/30) whilst the other end was joined to a 200 ml mercury reservoir. Contact to this mercury was made by means of a platinum wire sealed into the base of the reservoir. The reservoir and capillary could then be inserted through the cap of the cell into a corresponding female joint. When the apparatus was disconnected for purposes of cleaning or for changes of solution, the mercury capillary and reservoir could be removed for safe keeping by placing it in a long vertical glass cylinder fitted with a 10/30 female joint at the top. This cylinder may contain either dilute hydrochloric acid or simply conductivity water.

The top of the mercury reservoir was connected to a nitrogen gas line by means of a thin flexible spiral glass tube. The nitrogen line communicated to a cylinder of the gas, to a 2 litre reservoir, to one side of a 12 mm diameter mercury manometer, and to a Hoke valve and a stainless steel needle valve arranged in series with one another. The use of a 2 litre reservoir helps to stabilise the pressure readings

on the manometer. By manipulation of the two valves, with an excess pressure of nitrogen, the pressure could be finely controlled until the mercury in the capillary was just forced to its lower extremity, which was viewed by means of an 100 X magnifying monocular. It was also found that a gently tapering capillary contributed to the fineness of pressure control and the reproducibility of bringing the mercury to the same level at the extremity of the capillary. At the conclusion of this work, a binocular Bausch and Lomb "zoom" stereomicroscope became available which enabled vastly improved viewing of the capillary to be attained in "3-dimensions".

The pressure was read on the manometer by means of a cathetometer and the head of mercury from the bottom of the capillary to the upper level in the reservoir was similarly determined. The sum of these two heads² was the pressure required to maintain the mercury at the end of the fine capillary. Mercury height readings were corrected to standard pressure values using the appropriate density of mercury. Measurements were made at $26^{\circ} \text{C} \pm 1^{\circ} \text{C}$. The temperature of the apparatus was controlled by means of an internal glass coil situated within the compartments (not drawn on the schematic

² The variations of hydrostatic head due to the solution above the lower meniscus of mercury in the capillary were negligible and the head itself was small (0.5 cm.).

diagram of Figure VI) of the cell through which water at the required temperature was circulated by means of a pump from a thermostatted water bath located behind the cell as shown in the photograph (Figure V page 100). For accurate work it is important that the temperature of the mercury column should be constant since the density of mercury changes significantly with temperature such as in the measurements at 5° C, 25° C and 45° C of the heat of specific adsorption of iodide ions at mercury by Parsons and Anderson.¹⁰⁷ Ideally the whole apparatus should be enclosed within an insulated air box thermostatted at the desired temperature. However, this additional temperature control precaution need not be taken because it was shown that fluctuations in temperature of $\pm 1^\circ \text{C}$ did not significantly affect the measurements at 26° C. Moreover, an air box would hinder the ease of manipulation of the whole apparatus.

The diameter of the capillary at its end was calibrated using the surface tension data of Franklin and Joffe¹⁰² for hydrochloric acid at various concentrations, and that of Devanathan and Peries³⁰ for various concentrations of aqueous potassium chloride solutions. Surface tensions (γ) of mercury were calculated from the following relationship^{164a}

$$\frac{2\gamma}{r} = \rho gh \quad (99)$$

where r is the radius of the capillary, g the gravitational

constant and ρ the density of mercury at the cell temperature. Measurements of γ were taken at intervals of 50 mV. and after each measurement at a given potential a drop of mercury was forced out of the capillary before taking the next manometer reading in order to ensure a fresh surface. At each potential and in each solution, from three to five measurements of pressure were made by raising the pressure each time. The mean of these values was used in calculating the surface tension.

(iv) Electrical Measurements

Electrode potentials of the mercury were measured with respect to the calomel electrode using an high impedance Doran potentiometer with an external galvanometer which could be viewed simultaneously with the position of the mercury thread in the capillary. A range of potentials from zero to -1300 mV. with respect to the calomel electrode could be applied to the mercury by a system of switches and high resistances built into a box and placed, for convenience, close to the electrometer (see Figure V, page 100).

(v) Solutions

Hydrochloric acid solutions were made up from the redistilled constant boiling mixture using "equilibrium" water prepared by distillation of distilled water from alkaline

potassium permanganate in a still equipped with three spray traps. Solutions of hydrochloric acid made with once distilled water gave similar surface tension results.

Potassium chloride solutions were prepared from recrystallized analytical grade material. As in previous electrocapillary work³⁰ ultra-purification by pre-electrolysis was shown to be unnecessary. Trace impurities which may affect kinetic heterogeneous processes are thus generally less important in equilibrium electrochemical thermodynamic studies (cf. work on solid electrodes, Chapter IV). Bubbling of either purified hydrogen or nitrogen in the solution did not significantly affect the results and, in general, during measurements no gas was bubbled; more steady readings of pressure were then obtained and, with neutral solutions, loss of volatile solute, e.g. pyridine, by evaporation was thus avoided.

(vi) Organic Materials Used

The following organic bases were investigated: pyridine, 2-chloropyridine, 2-aminopyridine, 1,2,3,6-tetrahydropyridine, piperidine, aniline, quinoline and acridine. In addition, N-methyl pyridinium chloride and N-methyl-quinolinium chloride were examined. The initial materials were of high purity reagent grade (Eastman and Lights) and

were redistilled or recrystallised. In the case of quinoline, and of pyridine and its liquid derivatives, the distillation was carried out in nitrogen to avoid aerial oxidation. The final products used were rejected unless quite colourless. The purification of acridine and the preparation of the N-methyl quaternary salts were undertaken as described in Chapter IV. For work in neutral or acid solutions, the organic substances were made up to known concentrations in potassium chloride or hydrochloric acid solutions. After each run, the concentration of the organic solute in solution was checked where appropriate by a measurement of the ultra violet extinction on a Beckmann D.U. spectrophotometer using previously obtained calibration data. The highest concentrations of base studied in hydrochloric acid solutions were sufficiently low for it to be assumed from the known pK_a values that the quaternary ion was always present to an extent of over 99.99 per cent. There is thus no ambiguity as to their extent of ionisation.

(vii) Mercury

The mercury used for the electrocapillary studies was the "doubly-distilled" grade which was further purified by (a) anodic electrolysis in a mercurous nitrate-nitric acid solution; (b) washing in twice-distilled water and (c) redistillation "in vacuo" in an Hulett still with a capillary air lock.

CHAPTER III

PART I: ADSORPTION AT MERCURY

B. RESULTS

(1) Electrocapillary Curves

The electrocapillary curves for the bases present as ions in hydrochloric acid or as neutral molecules in potassium chloride solution are shown in Figures VII to XII (pages 111 to 116 inclusive) for various concentrations of the additives and at $26 \pm 1^\circ$ C. The values of the surface tension γ are plotted against the potential E of the mercury electrode measured against a calomel electrode in the same solution. Liquid junction potentials between the reference and mercury electrodes in solutions at high additive concentrations were hence avoided.

Values of γ could usually be determined between $E = 0$ and $E = -1200$ mV. At high negative potentials (less than -1000 mV.) values of γ were less reproducible than at lower potentials, as previously reported.^{63,31} This is probably due to the significant hydrogen evolution which occurs and to the corresponding discharge of the ions of the base (in the acid solutions). Usually three separate determinations of γ were made at each potential and concentration; at high negative potentials, five determinations

Figure VII: Electrocapillary curves for

a. Piperidine in N KCl

- | | |
|------------------------------|------------------------------|
| (1) IN HCl; | (2) $7.58 \times 10^{-3}M$; |
| (3) $2.27 \times 10^{-2}M$; | (4) $6.12 \times 10^{-2}M$; |
| (5) $1.50 \times 10^{-1}M$; | (6) $3.98 \times 10^{-1}M$. |

b. 1,2,3,6-tetrahydropyridine in N KCl

- | | |
|------------------------------|------------------------------|
| (1) IN HCl; | (2) $1.75 \times 10^{-3}M$; |
| (3) $8.75 \times 10^{-3}M$; | (4) $4.38 \times 10^{-2}M$; |
| (5) $9.14 \times 10^{-2}M$; | (6) $2.86 \times 10^{-1}M$; |
| (7) $7.43 \times 10^{-1}M$. | |

c. 2-aminopyridinium chloride in N HCl

- | | |
|----------------------------|----------------------------|
| ○ IN HCl; | • $4.34 \times 10^{-3}M$; |
| △ $5.20 \times 10^{-2}M$; | ▲ $1.13 \times 10^{-1}M$; |
| □ $3.40 \times 10^{-1}M$. | |

d. Pyridine in N KCl

- | | |
|------------------------------|------------------------------|
| (1) IN HCl; | (2) $2.35 \times 10^{-2}M$; |
| (3) $1.18 \times 10^{-1}M$; | (4) $3.10 \times 10^{-1}M$; |
| (5) $6.29 \times 10^{-1}M$. | |

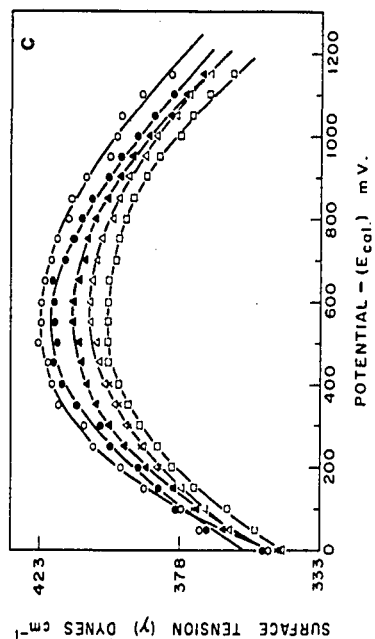
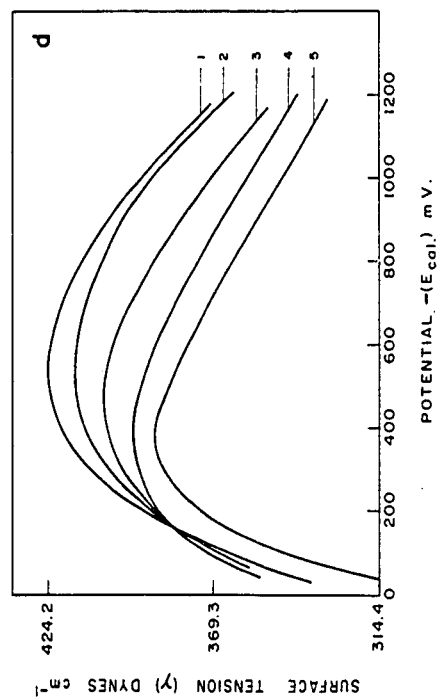
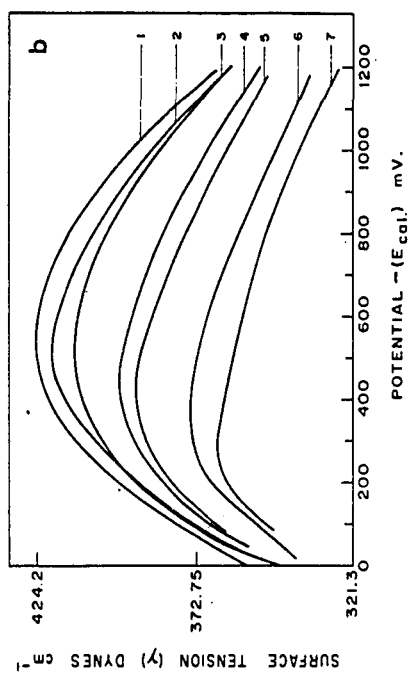
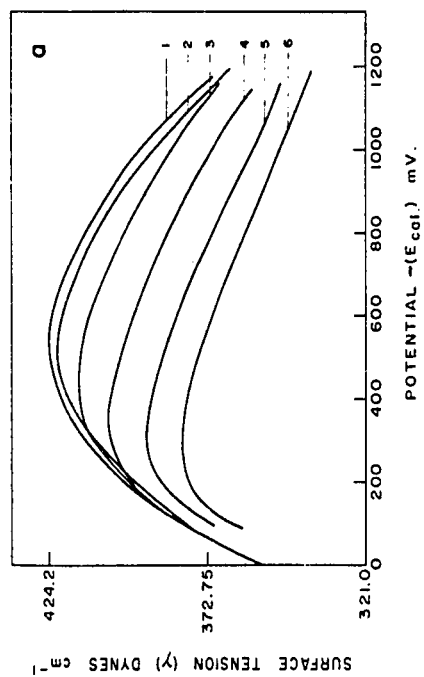


Figure VIII: Electrocapillary curves for

a. Aniline in N KCl

IN HCl;	0	$1.22 \times 10^{-3} M$;
$6.10 \times 10^{-3} M$;	X	$2.70 \times 10^{-2} M$;
$7.85 \times 10^{-2} M$;	A	$1.70 \times 10^{-1} M$.

b. Anilinium chloride in N HCl

Δ IN HCl;	A	$3.00 \times 10^{-3} M$;
0 $1.20 \times 10^{-2} M$;	0	$3.60 \times 10^{-2} M$;
X $1.01 \times 10^{-1} M$;	□	$4.00 \times 10^{-1} M$.

c. Pyridinium chloride in N HCl

• IN HCl;	0	$3.14 \times 10^{-3} M$;
X $1.57 \times 10^{-2} M$;	□	$9.42 \times 10^{-2} M$;
Δ $1.89 \times 10^{-1} M$;	A	$4.69 \times 10^{-1} M$.

d. Pyridinium chloride in N HCl

(1) IN HCl;	(2)	$9.00 \times 10^{-6} M$;
(3) $5.38 \times 10^{-5} M$;	(4)	$3.25 \times 10^{-4} M$;

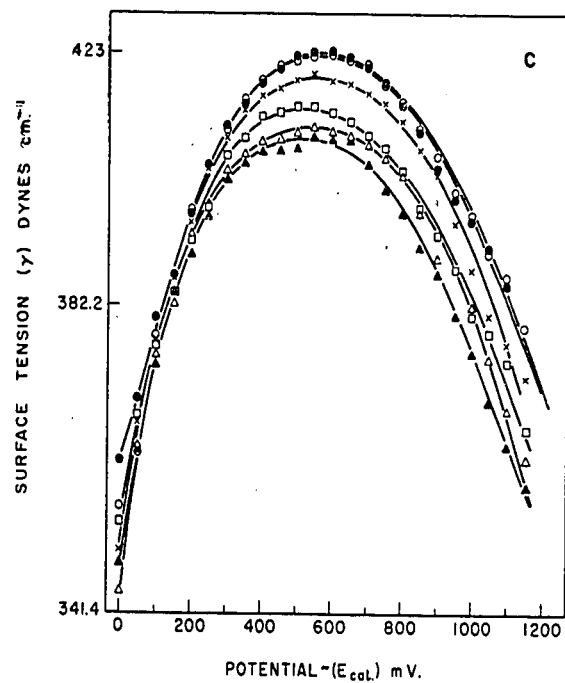
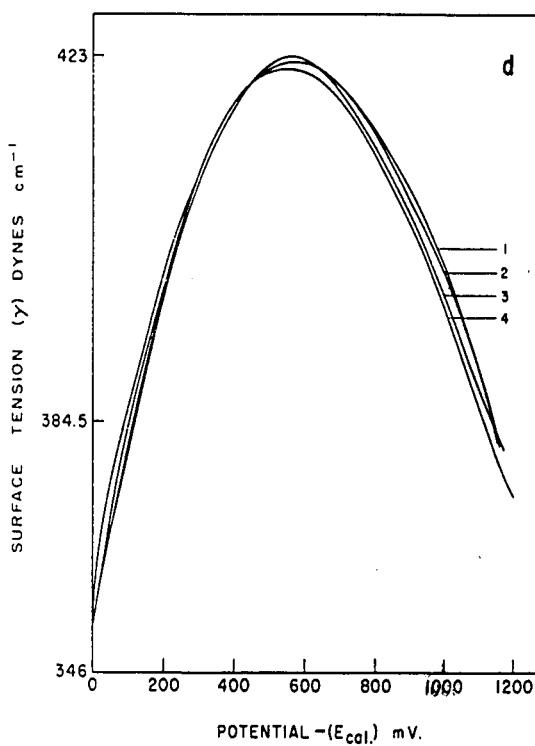
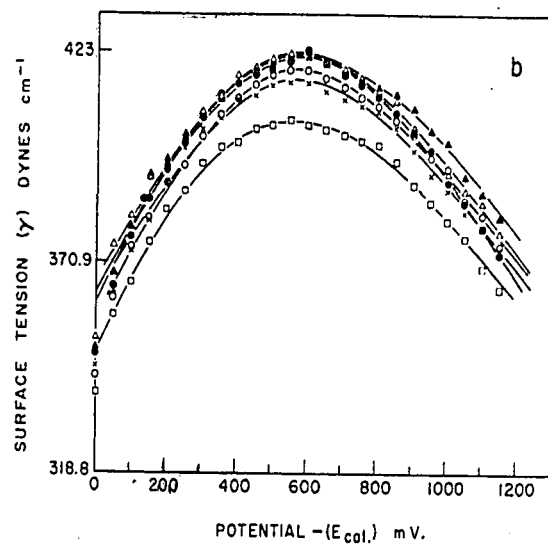
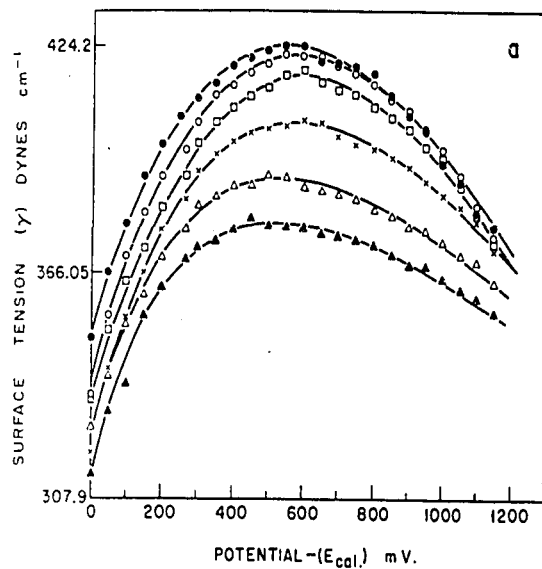


Figure IX: Electrocapillary curves for

a. Piperidinium chloride in N HCl

- | | |
|------------------------------|------------------------------|
| (1) IN HCl; | (2) $2.55 \times 10^{-2}M$; |
| (3) $7.96 \times 10^{-2}M$; | (4) $1.59 \times 10^{-1}M$; |
| (5) $5.50 \times 10^{-1}M$. | |

b. 2-aminopyridine in N HCl

- | | |
|----------------------------|----------------------------|
| ● IN HCl; | ○ $2.16 \times 10^{-3}M$; |
| x $3.72 \times 10^{-3}M$; | △ $3.05 \times 10^{-2}M$; |
| ▲ $1.17 \times 10^{-1}M$; | □ $2.92 \times 10^{-1}M$. |

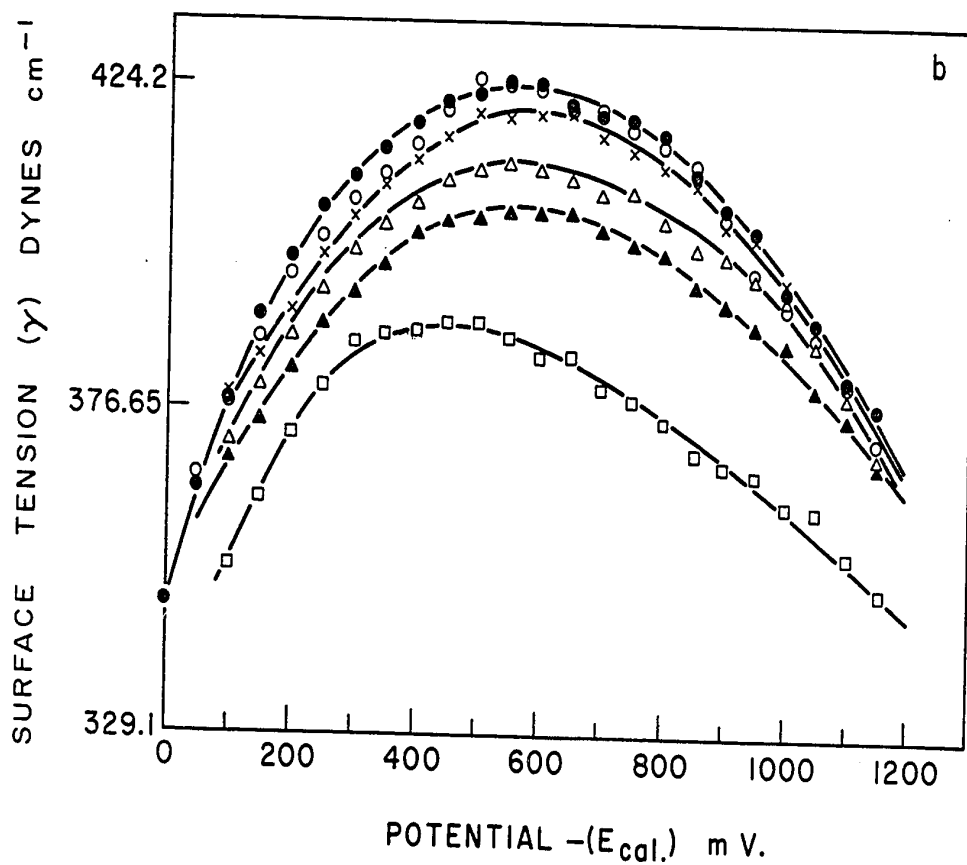
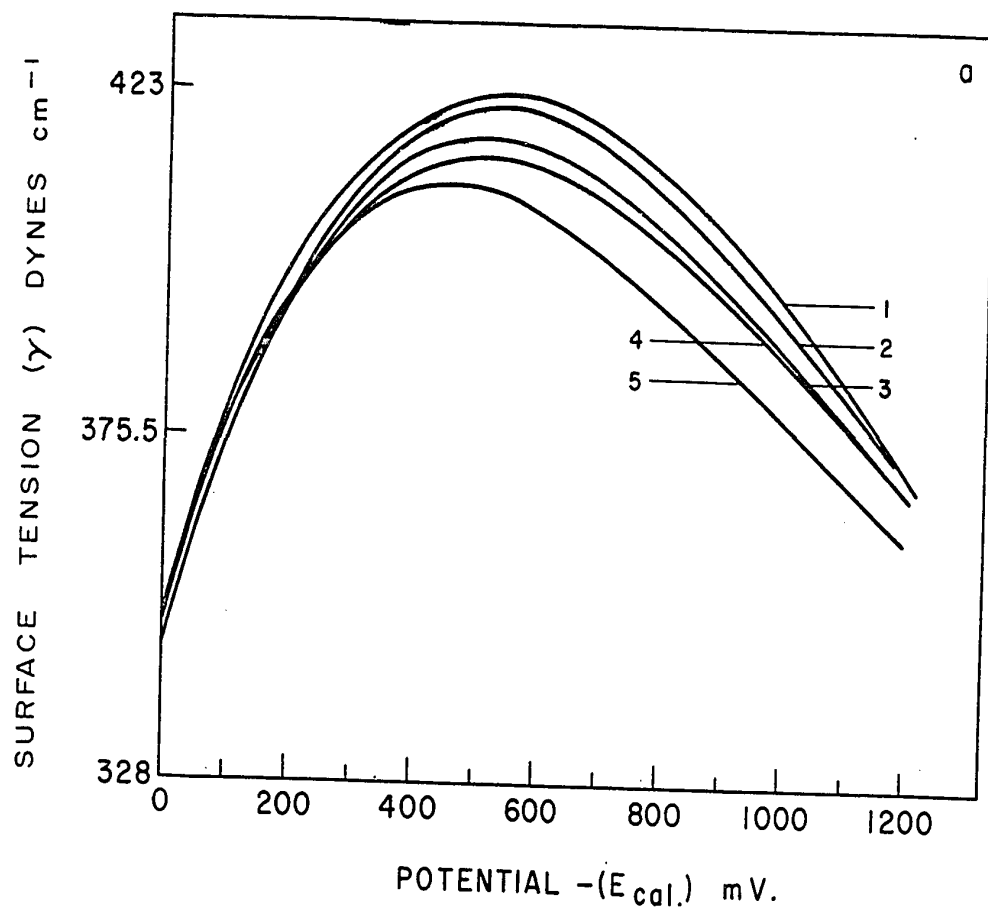


Figure X: Electrocapillary curves for

a. 2-chloropyridinium chloride in HCl

● IN HCl;	X	$3.02 \times 10^{-3}M$;
○ $7.50 \times 10^{-3}M$;	□	$3.02 \times 10^{-2}M$;
△ $7.50 \times 10^{-2}M$;	▲	$3.47 \times 10^{-1}M$.

b. 2-chloropyridine in HCl

○ IN HCl;	X	$8.60 \times 10^{-4}M$;
□ $2.64 \times 10^{-3}M$;	△	$8.80 \times 10^{-3}M$;
▲ $4.40 \times 10^{-2}M$.		

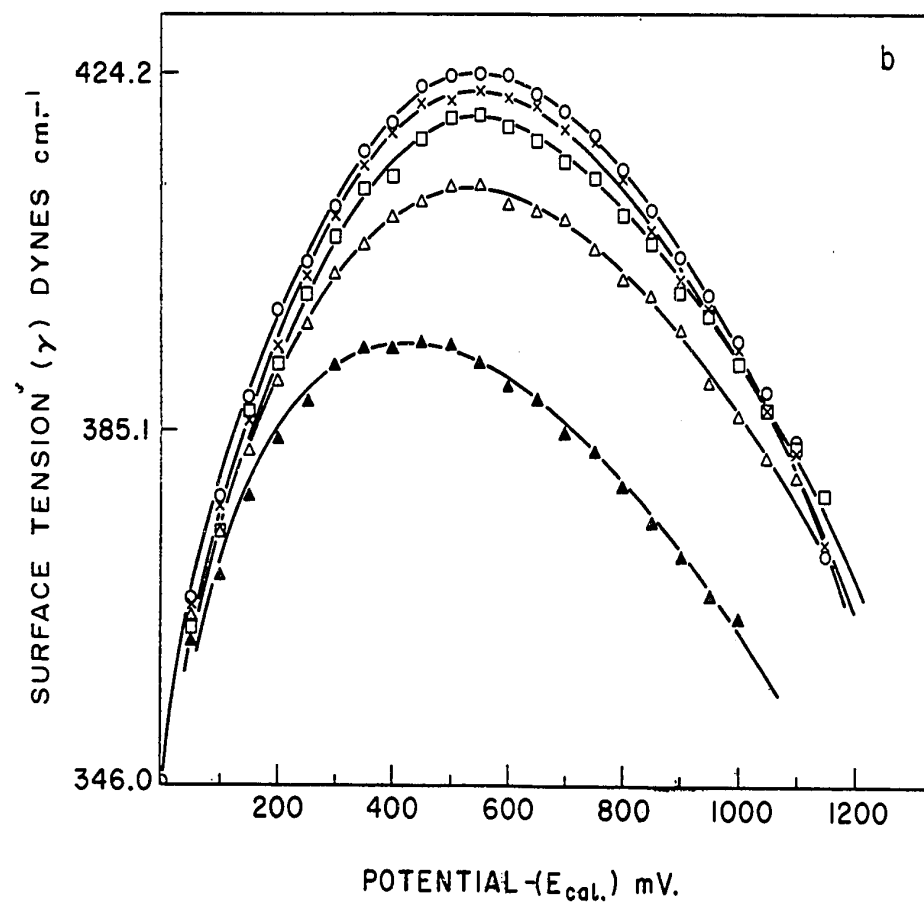
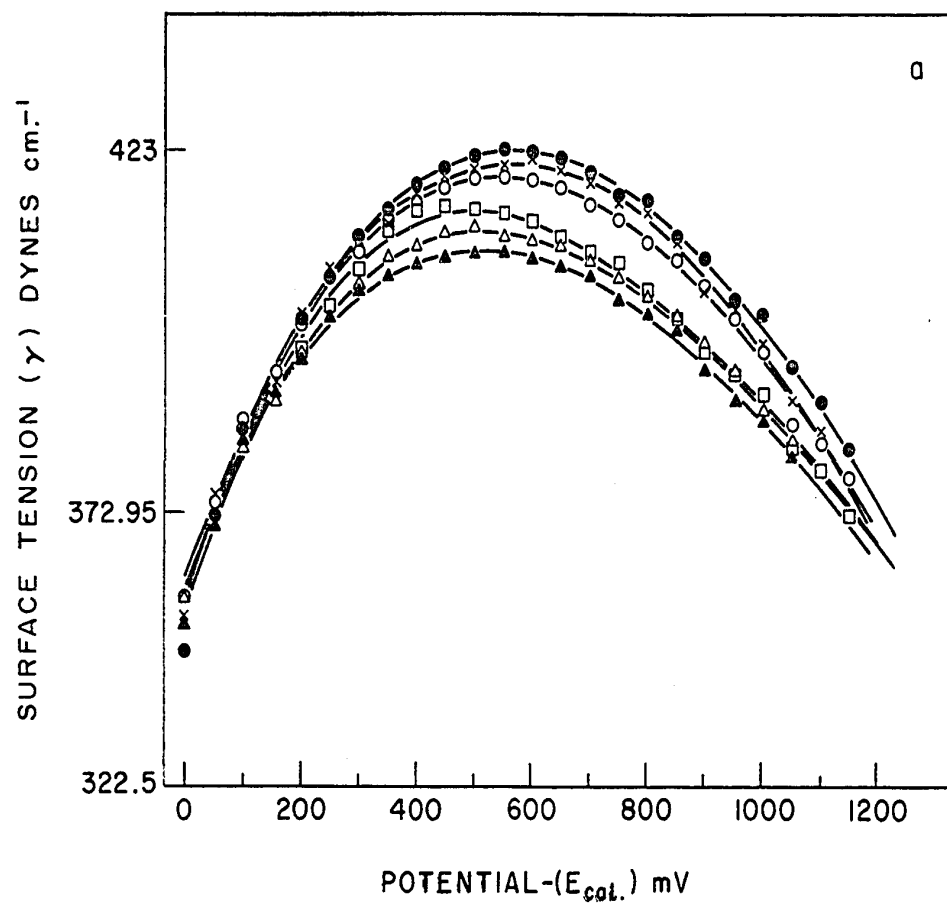


Figure XI; Electrocapillary curves

a. 1,2,3,6-tetrahydropyridinium chloride in N HCl

- 1N HCl; $\times$ $1.69 \times 10^{-3}M$;
- $8.43 \times 10^{-3}M$; $\square$ $4.22 \times 10^{-2}M$;
- △ $1.31 \times 10^{-1}M$; ▲ $4.09 \times 10^{-1}M$.

b. Pyridinium chloride in 0.1N HCl

- 0.1N HCl; $\times$ $3.18 \times 10^{-4}M$;
- $1.27 \times 10^{-3}M$; $\square$ $3.18 \times 10^{-3}M$;
- $1.07 \times 10^{-2}M$.

c. Pyridinium chloride in 0.33N HCl

- 0.33N HCl; Δ $7.13 \times 10^{-4}M$;
- $2.85 \times 10^{-3}M$; $\times$ $1.07 \times 10^{-2}M$;
- △ $3.21 \times 10^{-2}M$.

d. Pyridinium chloride in 5.0N HCl

- 5.0N HCl; Δ $6.12 \times 10^{-3}M$;
- $6.12 \times 10^{-2}M$; ▲ $2.45 \times 10^{-1}M$;
- $\times$ $4.91 \times 10^{-1}M$.

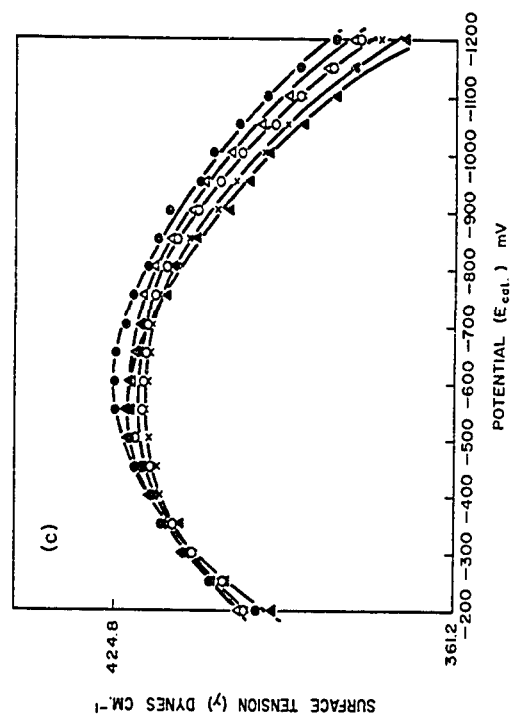
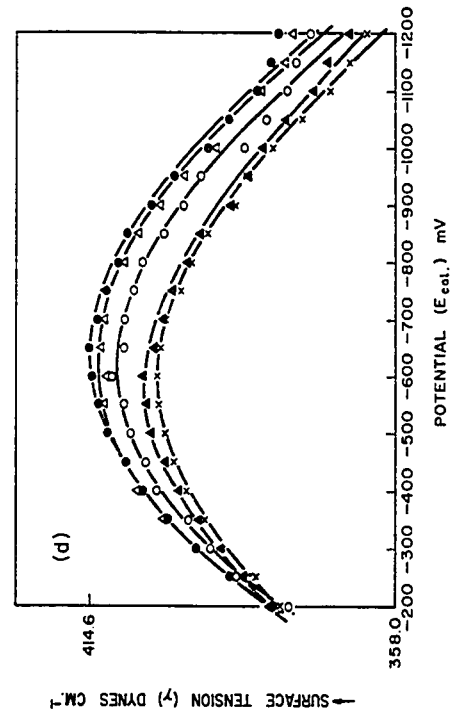
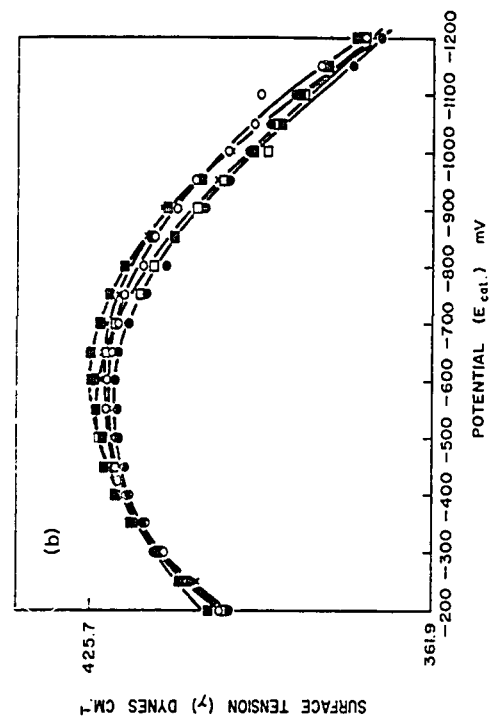
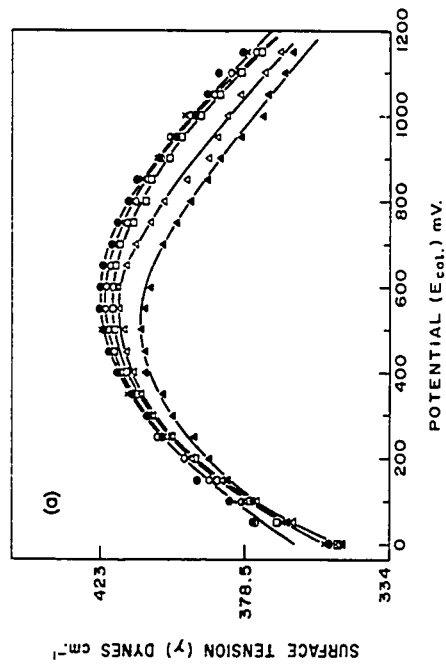
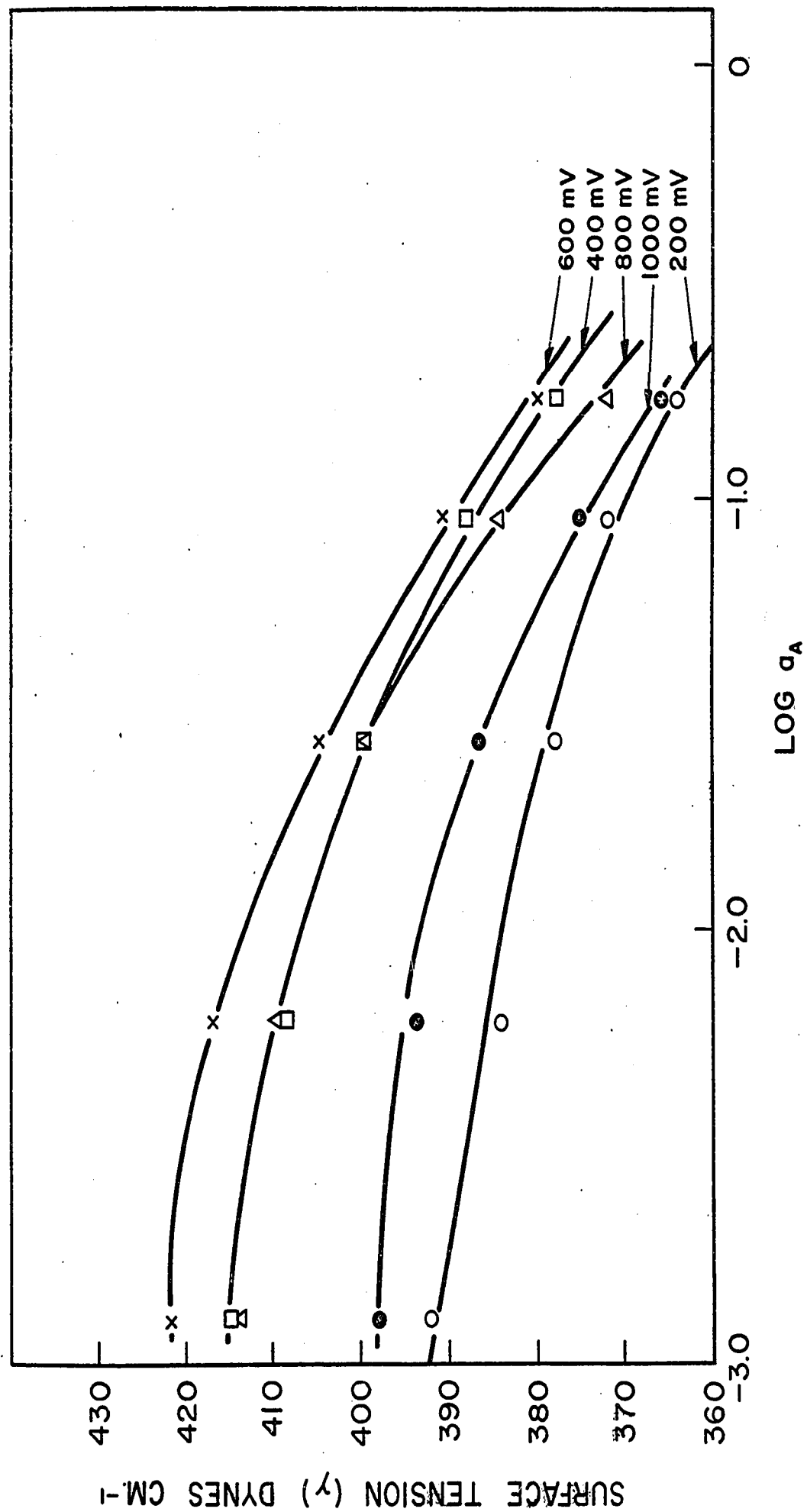


Figure XII: Plot of γ versus $\log a_A$ for the
evaluation of P_A .



were made. Reproducibility of excess pressure measurements was ± 0.02 mm. Hg up to $E = -600$ mV., about ± 0.03 mm. between $E = -600$ and -1000 mV. and about ± 0.1 mm. beyond this potential. Electrode potentials could be kept constant to better than ± 1 mV. Time variation of pressure readings at a given value of E was insignificant over periods of ten minutes except at the highest negative potentials where reduction of the base and evolution of hydrogen in the end of the capillary were no doubt responsible for the small variations observed (cf. "electrocapillary viscosity" reported by Butler and Cokrent⁶²).

(ii) Surface Excess and Adsorption Isotherms

The quantity of base or conjugate ion adsorbed at the electrode is expressed in terms of the surface excess Γ_A of the organic species and has been defined in Chapter I (pages 50-52). It will be noted from the thermodynamics (see Chapter I, pp. 50 et seq.) that Γ_A necessarily refers to both the quaternary ion BH^+ and the neutral base B . In acid solutions, however, where $a_{B^+} \gg a_B$ or a_{BH^+} the additive is almost entirely in the form B . The quantity Γ_A cannot be split up into Γ_B and Γ_{BH^+} without introduction of non-thermodynamic assumptions; however, in acid

solutions with $a_{H^+} \gg a_{BH^+}$, it may be anticipated that Γ_A will approximate closely to Γ_{BH^+} . In the case of quaternary salts, e.g. N-methyl pyridinium chloride, no ambiguity is involved since no proton equilibrium occurs. With pyridine, for example, having a pK_a value of 5.19¹⁶⁵ and at a concentration of 10^{-2} M, the concentration of pyridinium ions in 1.0 M HCl is some 3×10^5 times larger than that of pyridine molecules.

From the Gibb's adsorption equation Γ_A is obtained as

$$-(\partial \gamma / \partial \mu_A)_{T, \mu_{HCl}} = \Gamma_A \quad (100)$$

as discussed previously. Determinations of γ at various activities of the base or of its ions then give

$$-(\partial \gamma / RT \partial \ln a_A)_{T, \mu_{HCl}} = \Gamma_A \quad (101)$$

or a corresponding equation for measurements in potassium chloride solution where μ_{KCl} is kept constant.* The surface reference plane [of Chapter I, D (ii) and (iii), and C (i)] is chosen so that $\Gamma_{H_2O} = 0$ and the Γ_A values hence refer to amounts of organic solute adsorbed in the double layer as conventionally regarded. Γ_A is hence expressed as either

* A typical plot of γ versus $\log a_A$ (for aniline in N KCl solution) is shown in Figure XII⁴ (page 116).

** Evidence supporting this anticipation is discussed further in a later section of the thesis.

the corresponding charge $2F \Gamma_A$ μ -coulombs cm^{-2} or as moles cm^{-2} . When using equation (101) all results were referred to the electrocapillary curve obtained for the pure hydrochloric acid or potassium chloride solutions initially containing no additive (these are the so called "primitive" or "base" solutions in the terminology of electrocapillarity). In all runs, determinations of the initial electrocapillary curve for the pure salt or acid solution were made prior to addition of the organic solute. Adsorption isotherms were obtained by plotting values of Γ_A against concentration of the organic solute and are shown in Figures XIII to XV on pages 120 to 122.

In neutral solutions, the activities of the organic bases were assumed to be equal to their concentrations at the low concentrations used (less than ca. 0.01 M). The activity coefficients for the ionized bases were based on those for sodium toluene sulphonate¹⁶⁶ by using the datum for a solution of this salt at the appropriate ionic strength. Data for the "quaternary" (R^+) ions of pyridine and other bases used are unavailable and the organic toluene sulphonate ion is that most closely related in structure and size to those studied here. The above approximation is regarded as a desirable improvement on the assumption of unity³¹ for the activity coefficient of the organic ions, particularly for the higher concentrations of base in the acid solutions. We may observe that in using

Figure XIII: Adsorption isotherms at different
electrode potentials

- a. Piperidine in N KCl
- b. 1,2,3,6-tetrahydropyridine in N KCl
- c. Aniline in N KCl
- d. 2-Aminopyridine in N KCl

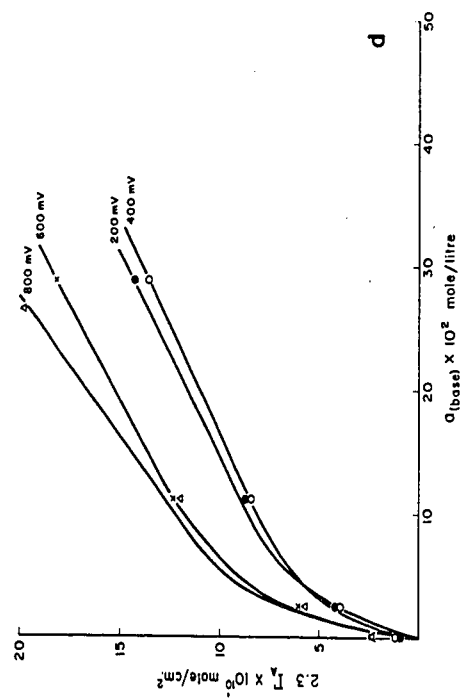
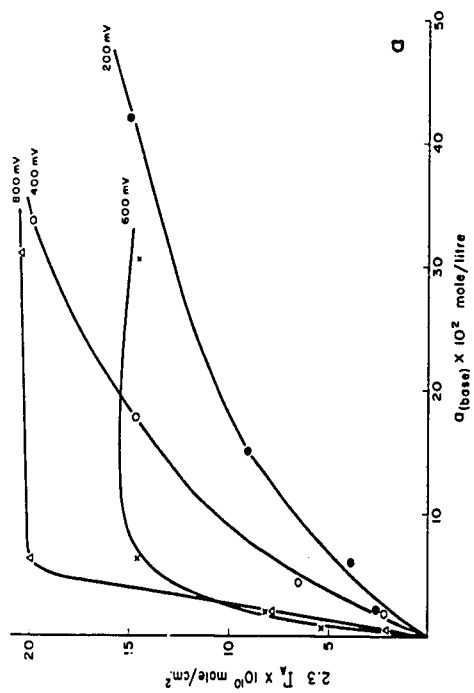
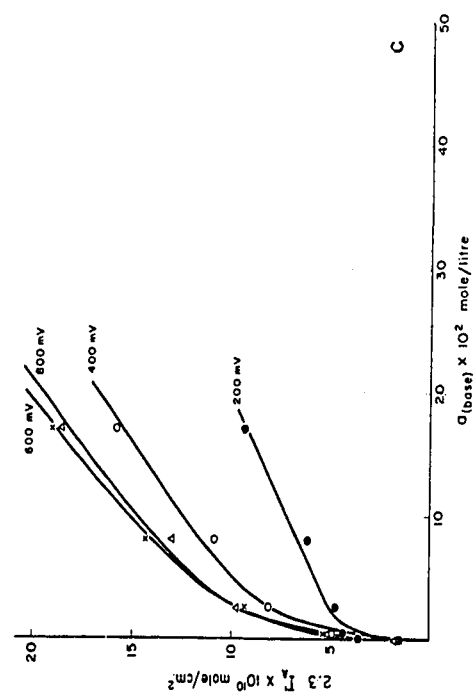
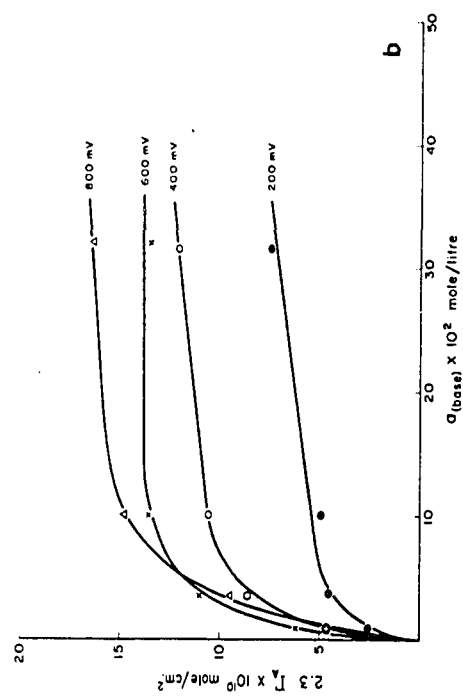


Figure XIV: Adsorption isotherms at different
electrode potentials

- a. 2-Aminopyridinium chloride in N HCl
- b. Anilinium chloride in N HCl
- c. 2-Chloropyridine in N HCl
- d. Pyridine in N HCl.

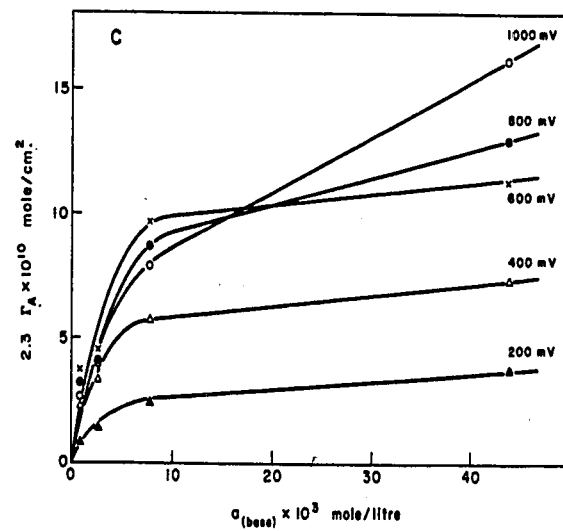
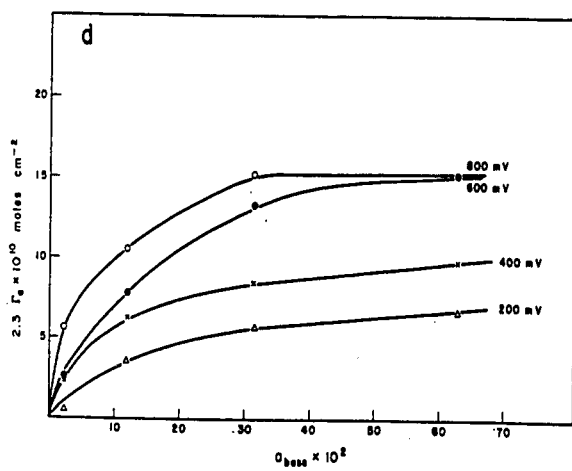
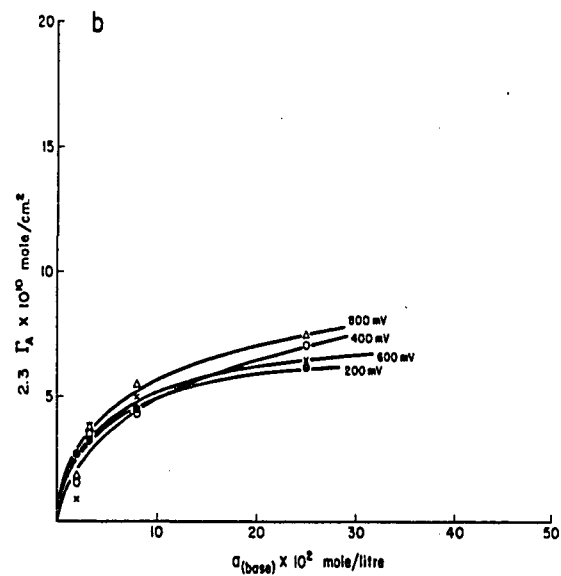
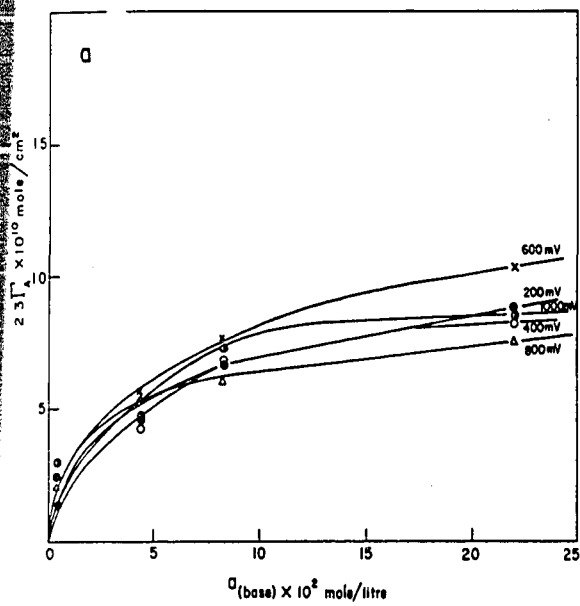
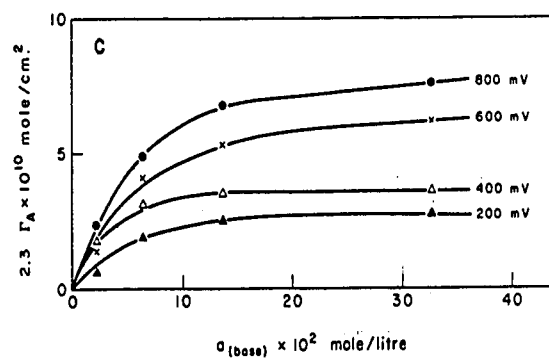
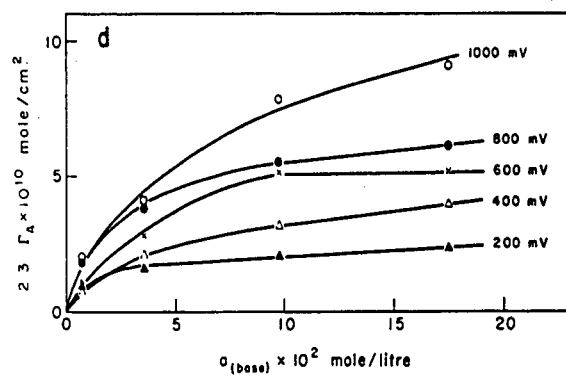
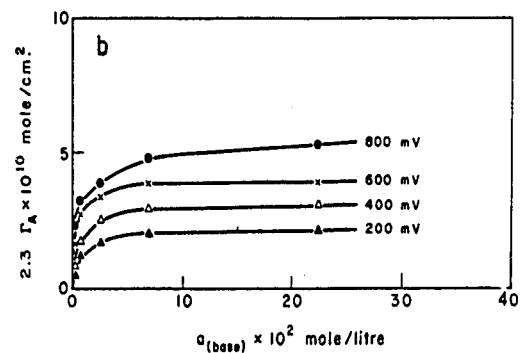
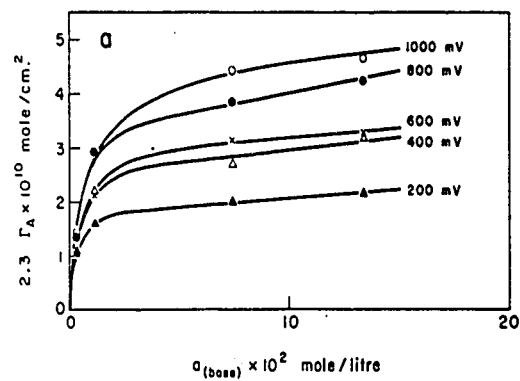


Figure XV: Adsorption isotherms at different
electrode potentials

- a. Pyridinium chloride in N HCl
- b. 2-Chloropyridinium chloride in N HCl
- c. Piperidinium chloride in N HCl
- d. 1,2,3,6-Tetrahydropyridinium chloride in N HCl.



the data for the toluene sulphonate salt instead of for "pyridinium" and related salts, little error will result since in the dilute solutions used the activity coefficients of various uni-univalent salts are not very dependent upon their structure.¹⁶⁷

(iii) Ionic Components of Charge

The ionic components of charge within the double layer may be determined by taking the following considerations into account. We can rewrite equation (80) (page 63) in the following manner.

$$q_+ = F \Gamma_+ = q_s - q_- \quad (102)$$

q_s is the total charge; q_+ and q_- represent the respective charges due to the total surface excess of positive ions and negative ions. The total charge q_s may be determined graphically from the slopes of the electrocapillary curves, since by rewriting equation (76) with respect to the calomel electrode,

$$\left(\frac{\partial \gamma}{\partial E_{\text{cal}}} \right)_{\mu_{\text{HCl}}, \mu_A} = q_s \quad (103)$$

Γ_+ may be obtained from equation (78) as discussed previously i.e.

$$\left(\frac{\partial \gamma}{\partial \mu_{\text{HCl}}} \right)_{E_{\text{cal}}, \mu_A} = - \Gamma_+ \quad (104)$$

It will be seen that Γ_+ follows from evaluating the slopes of $\Delta\gamma - \mu_{\text{HCl}}$ curves for constant potential with respect to the calomel electrode, and also for constant activity of A_2 , i.e. a_2 . According to the thermodynamic analysis which results in equation (30) we have seen that for an organic base, say pyridine, Γ_+ actually represents the sum $(\Gamma_{\text{BH}^+} + \Gamma_{\text{H}_3\text{O}^+})$ or $(\Gamma_{\text{Py}^+} + \Gamma_{\text{H}_3\text{O}^+})$, and that there are no thermodynamically valid means of evaluating either of the two quantities individually. Hence to satisfy the requirement in equation (104) that a_2 be constant, we must obtain surface tension values for constant ratios $a_{\text{BH}^+} : a_{\text{HCl}}$ (or $a_{\text{Py}^+} / a_{\text{HCl}}$). Therefore, $(\Delta\gamma)$ may be $a_{\text{Py}^+} / a_{\text{HCl}}$ interpolated from the electrocapillary curves at various concentrations of the base and hydrochloric acid, and plotted as a function of μ_{HCl} using the values of the mean activity coefficients for hydrochloric acid solutions $f_{\pm \text{HCl}}$ given by Harned and Owen.¹⁶⁸

The electrocapillary curves for varying concentrations of pyridine at four different concentrations of hydrochloric acid (0.1, 0.33, 1.0 and 5.0 N) are shown in Figures VII d and XI b, c and d. The actual values of $(\Delta\gamma)_E$, $a_{\text{Py}^+} / a_{\text{HCl}}$ may be interpolated from the plots of $(\Delta\gamma)_E$ against

$a_{Py} \sqrt{a_{HCl}}$; Γ_+ values are then calculated from the slopes of the curve $(\Delta \delta)_E$, $a_{Py} \sqrt{a_{HCl}} = -\log a_{HCl}$ using equation

(104), namely

$$\left(\frac{\delta \delta}{2.3 RT \delta \log a_{HCl}} \right)_{E_{cal.}} \mu_A = - \Gamma_+ \quad (105)$$

Having obtained q_s and q_+ (or $F \Gamma_+$), it is a simple matter to evaluate q_- (or $-F \Gamma_{Cl_-}$) since $q_s = q_+ + q_-$. Furthermore, $F \Gamma_A$ may be calculated from equation (101), and $F(\Gamma_{H_3O^+} - \Gamma_{Py^0})$

can be obtained* from equation (79). The five quantities, q_s , q_+ , q_- , $F \Gamma_A$ and $F(\Gamma_{H_3O^+} - \Gamma_{Py^0})$ may be graphically

plotted as a function of potential; such derived results will be presented, for convenience in the next Chapter (section C). By a similar set of calculations using electrocapillary curves obtained for varying adsorbate concentrations and varying acid concentrations, the components of charge as a function of potential for quinoline may be obtained.

The components of charge for solutions of N-Methyl pyridinium chloride in three hydrochloric acid solutions have also been evaluated from electrocapillary data. The calculations

* Here we are necessarily involved with the sum of two terms $\Gamma_{H_3O^+}$ and Γ_{Py^0} multiplied by the Faraday. It is evident that only the first has the clear physical significance of a charge.

are somewhat simpler than those for quinoline or pyridine in that the requirement for a_A to be constant is more easily achieved. It is unnecessary to interpolate surface tension values at constant ratios of $a_{\text{H}^+}/a_{\text{HCl}}$; N-methyl-pyridinium chloride is a fully ionised salt in solutions and the concentration of the positive ion, N-methyl-pyridinium (Me Py^+) is not dependent on the variation in activity of hydrochloric acid, since there is no proton equilibrium.

Finally the case of pyridine in neutral potassium chloride solutions has also been investigated and the components of charge determined.

(iv) Accuracy of Results

Systematic errors in related work have been discussed previously^{31, 63} and will apply almost quantitatively to the present data. The following differences from the previous work, however, give the present data (for acid solutions) somewhat lower systematic errors: (a) the use of a calomel electrode in the same solution, thus avoiding liquid junction potentials or local concentration e.m.f.'s between the reference and mercury electrodes; (b) corrections for interionic attraction effects in calculating μ_A . Overall systematic errors in γ_A are hence about 10 percent (cf. 31, 63) and will tend to be lower in the dilute solutions as the ratio a_{HCl}/a_A becomes larger.

Before proceeding to a quantitative description of the errors inherent in our experimental conditions, it would be appropriate at this point to mention the following factors; (1) reversibility of the calomel electrode in hydrochloric acid solution containing the organic ions was demonstrated by observation of the rapid recovery of the calomel electrode potential to the same steady values after temporary anodic or cathodic polarisation at 10^{-3} ampere cm^{-2} using an unpolarised electrode as reference; (2) an advantage of using the calomel electrode here is that upon introduction of the base into the acid solution the concentration of potential-determining ions (Cl^- in this case) is unchanged. If the hydrogen electrode is used, some of H_3O^+ ions are replaced by " RHH_3^+ " giving an unwanted change in the potential of the reference electrode for which corrections must be made.

(v) Quantitative Description of Experimental Errors

The value of a_{HCl} decreases as a result of addition of the organic base to the solution, therefore the constancy of μ_{HCl} in equations (101) and (103) is not exactly fulfilled. Correspondingly constancy of μ_A in equation (104) is obtained for a slightly different value of μ_{HCl} than if the concentration of H_3O^+ had remained unchanged. The error Δx may be expressed as follows:

$$\Delta X = \frac{\partial X}{\partial \mu_{HCl}} d\mu_{HCl} \quad (106)$$

where $X = q_s$, $F \Gamma_{Cl^-}$ or $F \Gamma_A$.

Since the original concentration of the hydrochloric acid is $C_{0,HCl}$, the concentration of the H_3O^+ ions in the cell decreases by an amount identical to C_{EH^+} in the final solution, i.e. it becomes $C_{0,HCl} - C_{EH^+}$, whereas the Cl^- concentration remains unchanged. Neglecting any changes in activity coefficients arising from the small change in H_3O^+ concentration the error becomes

$$\frac{1}{2} \frac{\partial X}{\partial \log C_{0,HCl}} d \log (1 - C_{EH^+}/C_{0,HCl}) \quad (107)$$

The errors are evaluated below for the maximum value of $[EH^+]/[HCl] = 0.1$, and without attention to sign. Since $d \log (1 - C_{EH^+}/C_{0,HCl}) = 0.046$, and the differential quotient in (107) for $q_s \leq 5 \mu\text{-coulombs cm}^{-2}$ per $\log C_{HCl}$ unit we find that the error in q_s i.e. Δq_s is equal to $\frac{5}{2} (0.046) = 0.1 \mu\text{-coulombs cm}^{-2}$. For $F \Gamma_{Cl^-}$ and $F \Gamma_A$ the differential coefficient in equation (107) did not exceed $24 \mu\text{-coulombs per log } C_{HCl} \text{ unit}$, hence $\Delta F \Gamma_A = \Delta F \Gamma_{Cl^-} = \frac{24}{2} (0.046) = \pm 0.55 \mu\text{-coulombs cm}^{-2}$.

Assuming that the inherent errors possess the same sign, we obtain for the total inherent error the following values given in Table 4.

Table V

<u>Experimental Errors</u>	
Δq_s	$= \pm 0.1 \mu\text{-coulombs cm}^{-2}$
$\Delta F \Gamma_{\text{Cl}^-}$	$= \pm 0.55 \mu\text{-coulombs cm}^{-2}$
$\Delta F \Gamma_A$	$= \pm 0.55 \mu\text{-coulombs cm}^{-2}$
$\Delta F(\Gamma_{\text{H}_3\text{O}^+} - \Gamma_A)$	$= \pm 1.3 \mu\text{-coulombs cm}^{-2}$
Δq_i	$= \pm 0.7 \mu\text{-coulombs cm}^{-2}$

The evaluations in Table V concern maximum possible systematic errors. Their significance in relation to the absolute values of experimental quantities clearly depends upon the magnitude of these. As an "order of magnitude" statement, the inherent errors in $F \Gamma$ and q values are $1 \mu\text{-coulomb cm}^{-2}$, and the mean order of magnitude of these quantities is about $9 \mu\text{-coulombs cm}^{-2}$, i.e. the systematic error has a mean relative magnitude of about 11 percent. This value is less than that of 15 percent shown by Blomgren and Bockris³¹ because in our system there are no errors arising from use of a reference electrode isolated from the compartment housing the capillary electrode. In Bockris and Blomgren's work the hydrogen reference electrode was not present in the

same solution as the capillary, but remained in the original hydrochloric acid solution. Therefore E_H , the potential of the mercury electrode versus the hydrogen electrode, differed from the ideal value by an amount corresponding to the difference in H_2O^+ concentration between the two solutions. This introduces additional errors in q and $\sqrt{}$ values as a result of the inconstancy of E_H .

CHAPTER IV

PART I: ADSORPTION AT MERCURY

DISCUSSION

A. ADSORPTION OF NEUTRAL ORGANIC BASES

(i) Preliminary Remarks

In Section A, the discussion will be limited to the adsorption of the neutral organic additives at mercury and Section B will be devoted to a comparative discussion of the adsorption of the conjugate ions. This will be followed by Section C which contains a commentary on the ionic components of charge in the electrical double layer. Finally, the Eads and Markov Effect for ionic and neutral organic additives will be examined in detail in Section D.

Although measurements of changes of surface tension or determinations of the surface excess of some neutral molecules have been made at the mercury electrode (loc. cit.), little attention has been paid to the nature of the adsorption isotherms and to their quantitative interpretation or to the detailed structure of the double layer in solutions of neutral molecules in electrolyte solutions.

(ii) Form of the Electrocapillary Curves in Neutral Solutions

Reference to Figures VII to XI indicates that with

all the cyclic bases studied, the variation of the lowering of surface tension $\Delta\gamma$ with E is qualitatively different from that found with aliphatic amines or acids.⁹³ Thus, although there is a relatively sharp desorption of the base at potentials anodic to the potential of the electrocapillary maximum, $E^{e.c.m.}$, there is continuous strong adsorption in all cases up to the highest negative values of E used, so that there is no sharp maximum in the adsorption of these compounds near the e.c.m. potential as there is for some aliphatic compounds.^{62,93}

With pyridine and its hydrogenated derivatives 1,2,3,6-tetrahydropyridine and piperidine, this tendency is maintained (Figures VII a, VII b, and Figures XIII and XIII b) and is hence not related to the aromatic or π -orbital character of the rings, although specific effects on the positive branch may be connected with π -orbital interaction with the electron-deficient mercury surface (see below).

The curves for both aniline and 2-amino pyridine (Figures VIII a and VIII b) show significantly greater symmetry than those for pyridine and its hydrogenated analogues. This difference arises mainly from the greater surface tension depression on the positive branch with the amino compounds. The dipole moments of the molecules (aniline $\mu = 1.51$ D.; 2-aminopyridine $\mu = 2.17$ D.; and pyridine $\mu = 2.23$ D.) cannot account for this behaviour through an interaction of the

molecular dipole with the electrode field since such an effect would be smaller for aniline, and about the same for 2-aminopyridine, compared with that for pyridine itself. With 2-chloropyridine ($\mu = 3.22$ D.), the electrocapillary curve is again more symmetrical than for pyridine, but in this case the higher dipole moment could lead to a relatively enhanced (electrostatic) adsorption on either side of the e.c.m. as discussed below in terms of the free energy of adsorption.

(iii) Electrostatic Effects

At various electrode potentials, the polarisation and dipole-field interaction energies, E_p and E_μ , respectively, will vary and cause changes of the surface excess of adsorbate and of the corresponding standard electrochemical free energy of adsorption with electrode potential ϕ_p measured with respect to $\text{N}^{\text{H}}\text{C}^{\text{H}}\text{E}$. The substances studied have various dipole moments and polarisabilities, and the values of E_μ and E_p at $\phi_p = 0.2, 0.4$ and 0.6 volt are given in Table VI (page 134), assuming that in the 1N hydrochloric acid or potassium chloride solutions used the potential drop across the Helmholtz layer due to excess coulombic surface charge is approximately equal to ϕ_p . These values are calculated assuming the molecular dipole is normal (but see below) to the mercury surface [cf. Pierst et al.³⁶], i.e. assuming that the local force field is

TABLE VI

Substance	$\alpha \times 10^{24}$ cc.mole ⁻¹	μ , D	p cal. mole ⁻¹		
			$\phi_F=0.2$	$\phi_F=0.4$	$\phi_F=0.6$
Pyridine	9.9	2.23	20	79	178
2NH ₂ -Pyridine	11.1	2.17	22	89	199
2Cl-Pyridine	11.7	3.22	24	94	211
Piperidine	9.3	1.17	19	74	173
Aniline	11.1	1.51	22	89	199
Benzene	9.8	0	20	79	177
Water	1.44	1.87	3	11	26

Continued on next page

TABLE VI (Continued)

Substance	E cal. mole ⁻¹		E total cal. mole ⁻¹		Dipole Image Potential
	$\phi_F=0.2$	$\phi_F=0.4$	$\phi_F=0.2$	$\phi_F=0.4$	
Pyridine	535	1070	555	1150	150
2NH ₂ -Pyridine	520	1040	542	1130	140
2OL-Pyridine	772	1540	796	1630	310
Piperidine	201	562	300	636	40
Aniline	362	724	394	813	60
Benzene	0	0	20	79	0
Water	449	698	452	909	100

1. Values of χ are from refs. (170 to 172) or calculated by standard additivity principles.
2. Values of μ are from refs. (86), (165) and (173).
3. E_p and E_m are given to 3 significant figures but the assumption that the field is approximately $\Delta\phi_F/\delta$ with $\delta = \frac{1}{2} 4\text{\AA}$ renders the values given significant only to 2 figures.
4. The dipole image potential (174) is calculated for perpendicular orientation to the metal. It will be 0.5 times this value for "flat" orientation.

sufficient to make the energy of the dipole in the field much greater than kT . Electrostatic contributions to the energy of water molecules of the interface are also recorded. Upon adsorption of a molecule of projected surface area A , A/a water molecules must be desorbed (if a is the projected area of H_2O) with a gain in energy [cf. Butler⁹³] of $\frac{A}{a} U_{H_2O}$: if U_{H_2O} is the adsorption energy of one water molecule. The relative magnitudes of the theoretical electrostatic energy effects including image potentials are summarised in Table VI (pages 134, 135).

(iv) The Adsorption Isotherms

In this section, the discussion is confined to the results for neutral molecules and the comparison with those for the conjugate ions is referred to in section B of this Chapter. The electrocapillary data lead to adsorption isotherms at various constant electrode potentials and the isotherms can be treated thermodynamically in a formal way exactly analogous to that previously given for adsorption of ions,³¹ whereupon the Langmuir isotherm can be written in the following form:

$$\ln \left[\frac{55.5}{C_A} \cdot \frac{\theta}{1-\theta} \right] = - \Delta \bar{G}^0 / RT \quad (108)$$

where $\Delta \bar{G}^0$ is the standard electrochemical free energy of adsorption of the base A at a concentration C_A corresponding to a fractional surface coverage of θ . $\Delta \bar{G}^0$ in fact represents the difference of standard electrochemical free energies of adsorbate and solvent referred to standard states of unit mole fractions of adsorbate and water in solution and unit surface mole fractions of these components in the surface phase.

The derivation of equation (108) will be given in detail* below because of its importance in the interpretation of the adsorption behaviour to be discussed in this part of the thesis. The deduction of (108) involves the assumption of no interaction between molecules in the adsorbed layer. If the adsorption of A is considered to be "ideal" (zero interaction between adsorbed species), no activity coefficient appears in the expression for $\bar{\mu}_A^s$ (the electrochemical potential of A in the surface layer) which may be written

$$\bar{\mu}_A^s = \bar{\mu}_A^{o,s} + RT \ln \theta \quad (109)$$

* In the original derivation published by Bockris and Blomgren³¹ two important typographical errors have been overlooked in the equations. These errors are corrected in the present treatment.

where $\bar{\mu}_A^s$ is the electrochemical potential^{*} of the adsorbed entity, A, $\bar{\mu}_A^{0,s}$ represents the standard electrochemical potential referred to a standard state of unit surface mole fraction and θ as mentioned above is the fraction of the surface covered with A.

For water adsorbed on the electrode, and for conditions such that specific adsorption of other substances than water and the organic additive is negligible

$$\bar{\mu}_{H_2O}^s = \bar{\mu}_{H_2O}^{0,s} + RT \ln (1 - \theta) \quad (110)$$

where $\bar{\mu}_{H_2O}^{0,s}$ is the chemical potential of the adsorbed water referred to a surface mole fraction of unity. Correspondingly for A and H_2O in the solution we can

* This term will also strictly apply to neutral polar adsorbed species where an electrostatic field polarisation energy of $1/2(\alpha_0 + \frac{D^2}{3kT})E^2$ contributes to $\bar{\mu}_A^{0,s}$, α_0 and D being the polarisability and dipole moment, respectively. The thermodynamics of dipolar molecules in fields, as treated in Guggenheim's monograph, can be conveniently examined in terms of such electrochemical potentials.

write

$$\bar{\mu}_A^s = \bar{\mu}_A^{o,s} + RT \ln a_A^s \quad (111)$$

where $\bar{\mu}_A^s$ is the electrochemical potential of A in solution and $\bar{\mu}_A^{o,s}$ is the standard electrochemical potential of A referred to unit mole fractions; and

$$\mu_{H_2O}^s = \mu_{H_2O}^{o,s} + RT \ln a_{H_2O}^s \quad (112)$$

where $\mu_{H_2O}^s$ is the chemical potential of water in solution and $\mu_{H_2O}^{o,s}$ is the standard chemical potential of water referred to a standard state of unit mole fraction of water in solution. Now since

$$\bar{\mu}_A^s - \mu_{H_2O}^s = \bar{\mu}_A^{o,s} - \mu_{H_2O}^{o,s} \quad (113)$$

and denoting the difference in standard electrochemical free energy of adsorption of adsorbate and water by $\Delta \bar{g}^o$

$$\Delta \bar{g}^o = (\bar{\mu}_A^{o,s} - \mu_{H_2O}^{o,s}) - (\mu_{H_2O}^{o,s} - \mu_{H_2O}^{o,s}) \quad (114)$$

By expanding (114), using the relationship in (113) and cancelling terms we arrive at

$$-\Delta \bar{G}^0/RT = \ln \left[\left(\frac{\theta}{1-\theta} \right) \cdot \frac{a_{H_2O}^s}{a_A^s} \right] \quad (115)$$

The rational activity a_A^s of A in a dilute solution can be expressed approximately in terms of C_A , the molar concentration, by the following equation¹⁶⁹

$$a_A^s = \frac{M_{H_2O} C_A}{1000 \rho_{H_2O}} \cdot f_A^s \quad (116)$$

where M_{H_2O} and ρ_{H_2O} are the molecular weight and density of water respectively and f_A^s is the activity coefficient of A at the concentration C_A .

Hence (115) now becomes

$$-\Delta \bar{G}^0/RT = \ln \left[\frac{\theta}{1-\theta} \cdot \frac{55.5}{C_A f_A^s} \right] \quad (117)$$

which is identical with (108) except for the activity coefficient f_A^s . If this is unity, equation (117) reduces exactly to (108) and is equivalent to a Langmuir isotherm.

When surface interactions occur, we would have to

use (109) with a surface activity coefficient f_θ in the ln so that (117) would then be written as

$$\ln \left[\frac{\theta}{1-\theta} \cdot \frac{55.5}{C_A} \right] + \ln f_\theta = - \Delta \bar{G}^\circ / RT \quad (118)$$

Any deviations from (108), the Langmuir isotherm, will appear as an apparent variation of $\Delta \bar{G}^\circ$ with coverage or, in equation (118) are expressed by the term $RT \ln f_\theta$ at various values of θ where f_θ can be written in terms of $(G_{11})_\theta$, the "non-ideal" free energy of interaction of the adsorbate dipoles at the coverage θ . It is evident that the term f_θ will be

$$f_\theta = \exp[-(G_{11})_\theta / RT] \quad (119)$$

(v) Evaluation of $\Delta \bar{G}^\circ$ at Various Electrode Potentials

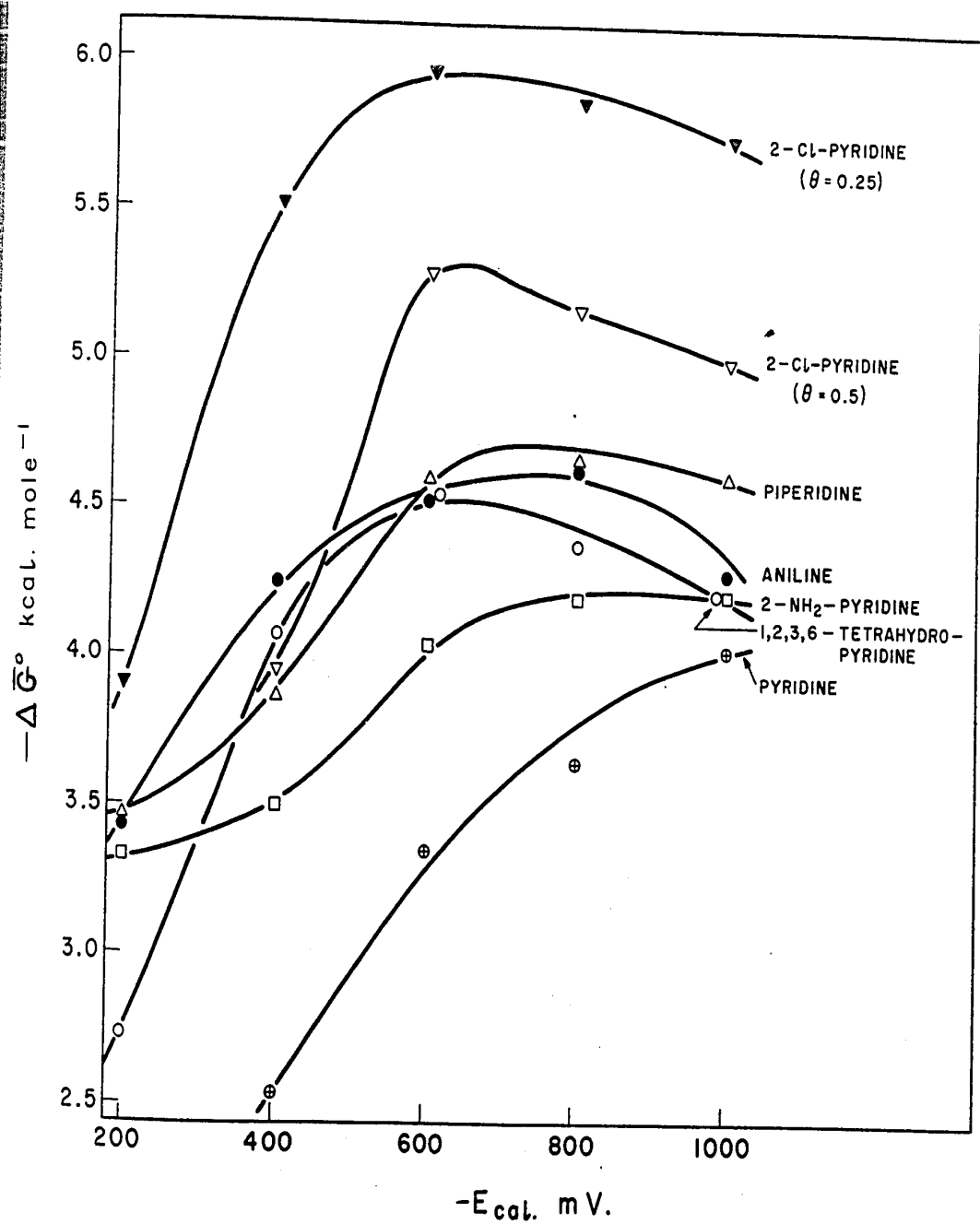
From Figures XIII, XIV and XV we may convert Γ_A values into corresponding θ values using values of the maximum surface excess $\Gamma_{A,max.}$ for a monolayer of adsorbate molecules. The value of θ thus calculated will depend on (i) the orientation of the molecules at complete coverage and (ii) the projected effective area for the molecule relevant to that orientation. For neutral bases, the observed $\Gamma_{A,max.}$ values correspond most closely to adsorbed dipoles of the bases standing perpendicularly to the surface, (as also deduced by Gierst et al.⁸⁶) using values of the projected molecular areas derived from measurements on large scale Courtault atomic models.

At various concentrations and potentials, θ can be determined and hence $\Delta \bar{E}^0$. Values of $\Delta \bar{E}^0$, the change of standard electrochemical potential, at $\theta = 0.5$ are shown in Figure XVI (page 143) as a function of electrode potential. In all cases $\Delta \bar{E}^0$ is not symmetrical about the e.c.m. potential, being relatively lower on the anodic branch than on the cathodic probably owing to preferential solvation of the electronegative ends of the X-containing molecules by water when they are oriented with the lone pair of electrons on X outwards from the mercury on the negative branch [cf. reference (86)]. At anodic potentials, $\Delta \bar{E}^0$ falls off, probably owing to preferential adsorption of the smaller polar solvent molecules,⁹³ to increasing population of the double layer by specifically adsorbed chloride ions and to reorientation of the adsorbate as discussed above. π -orbital effects and comparisons with $\Delta \bar{E}^0$ values for the conjugate ions will be discussed in section E of this chapter.

(vi) Interaction Effects between Adsorbed Dipoles

These will be investigated by evaluating $\Delta \bar{E}^0$ as a function of θ and deducing the nature of f_θ in equation (119); here, to a first approximation, G_{11} will be composed of (i) an electrostatic dipole-dipole interaction term dependent on

Figure XVI: Values of $\Delta \bar{G}^0$ ($\theta = 0.5$) for the
organic bases as a function of
electrode potential E_{cal} .



the average orientation of, and separation r between, the molecules in the interface; and (ii) a Van der Waals-London interaction term.⁹² G_{11} may hence be written per mole (N) of molecules in the surface layer with coordination number z as approximately⁹

$$G_{11} = \frac{1}{2} Nn \bar{\phi}_{11} \quad (120)$$

where

$$\bar{\phi} = \frac{\mu^2}{\epsilon_s r^3} - \frac{B}{\epsilon_0 r^6} \quad (121)$$

for dipoles oriented normally⁹² to the surface, and μ is the dipole moment of the solute molecule, ϵ_s the dielectric constant of the surface layer, ϵ_0 the electronic dielectric constant³¹ in the surface layer and B the Van der Waals-London

* Here we assume with Mitchell¹⁷⁵ that the electrostatic potential energy of interaction of the dipoles is the main factor determining G_{11} ; orientation entropy effects are relatively negligible. (See "Statistical Thermodynamics", Terrell Hill Addison-Wesley, 1960, p. 209).

** When the dipoles are oriented at various angles in space, the electrostatic components of $\bar{\phi}_{11}$ become⁹, for two dipoles A and B,

$$\bar{\phi}_{11} = \frac{\mu^2}{\epsilon_s r^3} \left[2 \cos \beta_A \cos \beta_B - \sin \beta_A \sin \beta_B \cos(\gamma_A - \gamma_B) \right]$$

where β_A and β_B are angles of inclination of components of the dipoles in the surface and γ_A and γ_B are the angles of inclination of the dipoles to the surface. Under these general conditions the result for the average interaction energy is mathematically intractable (cf. Mitchell¹⁷⁵) but is soluble for a completely oriented monolayer, as assumed here, where the interactions between the solute dipoles are all repulsions.

coefficient. The quantity B originally given by London's equation, is now regarded as being represented better by

$$B = \frac{3}{4} \sqrt{sz} \ h \gamma_0 \alpha^2 \quad (122)$$

where s is the effective number of optical dispersion electrons, z the number of electrons in outermost electron shells of the molecule and α the electronic polarizability; empirically¹⁷² $s/z \doteq 0.39$ so that

$$B = 0.47 z \ h \gamma_0 \alpha^2 \quad (123)$$

and¹⁷²

$$\gamma_0 = 2532 (\alpha)^{-1/2} \quad (124)$$

Noting that

$$A = \pi R^2, \ r = \sqrt{A/\pi}, \ \alpha \doteq R^3$$

where R is the "radius" of the organic adsorbate of area A , we obtain

$$\phi_{11} = \frac{\mu^2 \epsilon^{3/2}}{\sum_s \pi^{3/2} R^3} = 1190 \frac{z \ h \ \epsilon^3}{\sum_0 \pi^3 R^{3/2}} \quad (125)$$

(the dipole term can also be conveniently kept in the form $\mu^2 \epsilon^{3/2} / \sum_s A^{3/2}$). The quantity ϕ_{11} should hence vary linearly with $\epsilon^{3/2}$, or the calculated apparent $\Delta \bar{G}^0$ values should decrease linearly with $\epsilon^{3/2}$ (except as $\epsilon \rightarrow 1$ when the attractive forces become significant).

Tests of equation (120) using ϕ_{11} from equation (125) are shown for 2-chloropyridine, 1,2,3,6-tetrahydropyridine,

pyridine, and 2-aminopyridine and aniline in Figures XVII a, b and XVIII a, b. In these Figures $\Delta \bar{G}^0$ is plotted against $\theta^{3/2}$ only. The dispersion term in θ^3 only becomes significant if $\theta > \text{ca. } 0.6$ with μ in the surface layer taken about twice its normal value [see below: page 152, references (175, 176, 177)]. The validity of the plot in $\theta^{3/2}$ alone is demonstrated a posteriori by the absence of a minimum in $\Delta \bar{G}^0$ except for aniline, and then only at the highest values of $\theta^{3/2}$.

For pyridine and its derivatives these Figures show, in fact, that $\Delta \bar{G}^0$, and hence $\Gamma_{A,1}$, varies in the theoretically expected way with $\theta^{3/2}$; there is, however, a remarkable sharp break in most of the curves except in those for the least " π -deficient"¹⁶⁵ molecules, 2-aminopyridine and aniline. In assessing these results, we may note that no other function of θ (e.g. $\theta^{1/2}$, θ^2) represents $\Delta \bar{G}^0$ so well, giving definite linear regions, as that based on $\theta^{3/2}$, the theoretically predicted dependence on θ . The sharp inflexions in the $\Delta \bar{G}^0 = \theta^{3/2}$ lines are also not the result of any (inevitable) arbitrariness in the choice of the $\Gamma_{A,\text{max}}$ values. For 2-chloropyridine the same kind of line (e.g. at -400 mV.), but displaced to higher $\Delta \bar{G}^0$ values, is obtained if we take $\Gamma_{A,\text{max}} = 5.2 \times 10^{-10}$ rather than 7.4×10^{-10} mole cm^{-2} (see Figure XVII a) - the value for perpendicular orientation.

Figure XVII:

- a. Plots of $\Delta \bar{G}^0$ vs $e^{3/2}$ for 2-chloropyridine in N KCl at various electrode potentials. Solid lines for $\Gamma_{\text{max.}} = 7.4 \times 10^{-10}$ mole cm^{-2} , dotted line for $\Gamma_{\text{max.}} = 5.2 \times 10^{-1}$ mole cm^{-2} ,
- b. Plots of $\Delta \bar{G}^0$ vs $e^{3/2}$ for 1,2,3,6-tetrahydropyridine and for pyridine in N KCl at various electrode potentials.

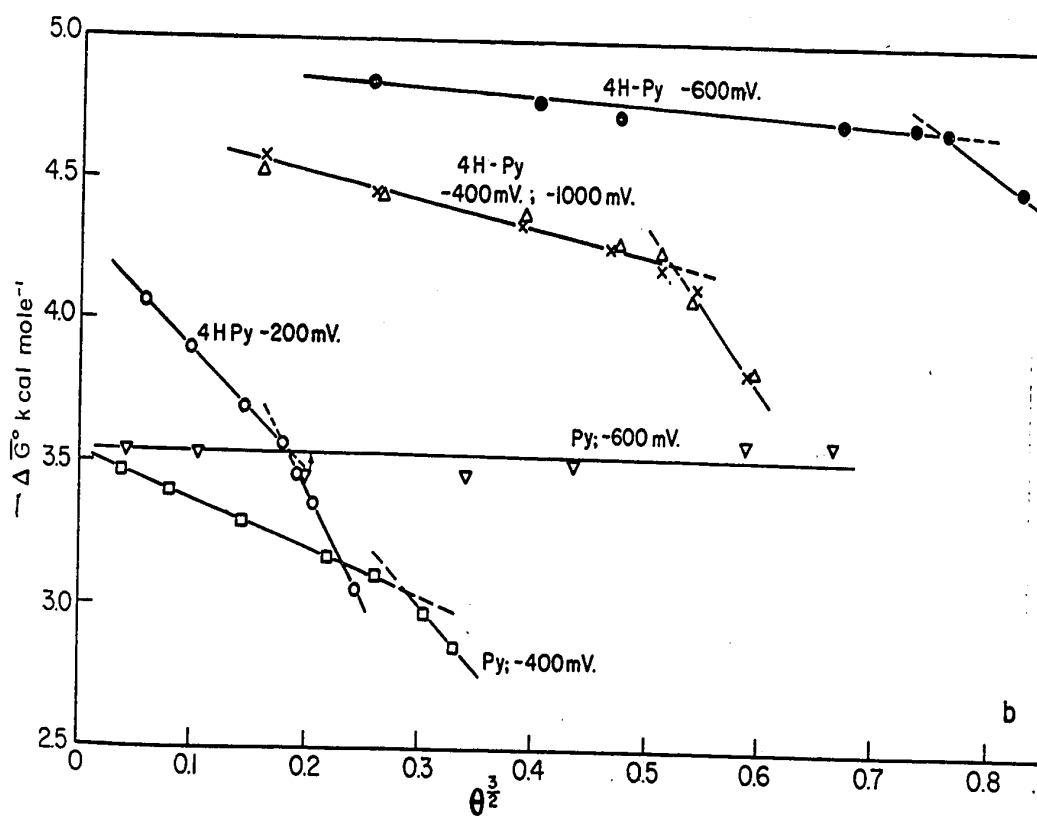
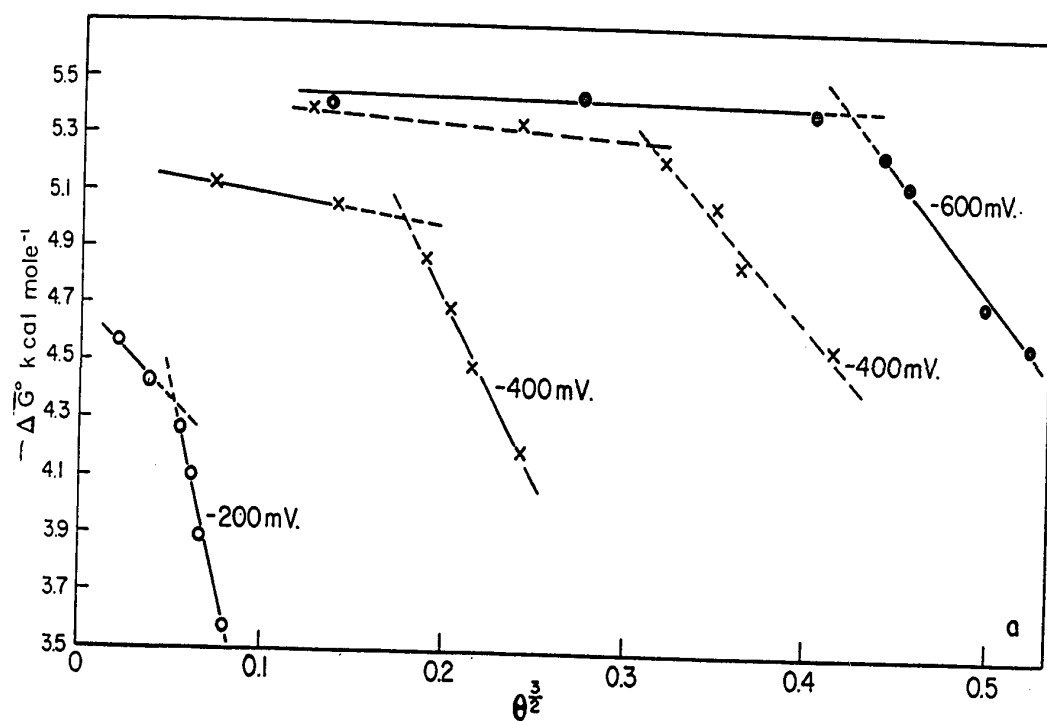
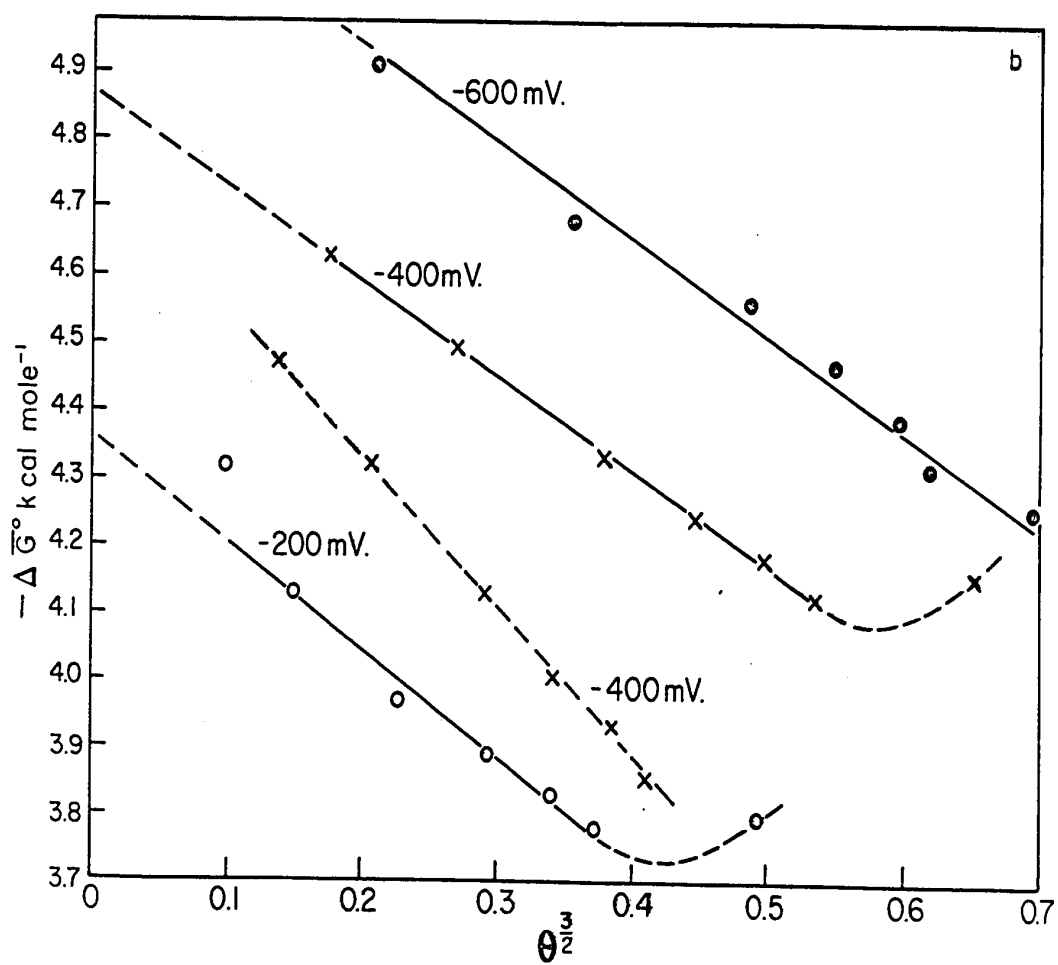
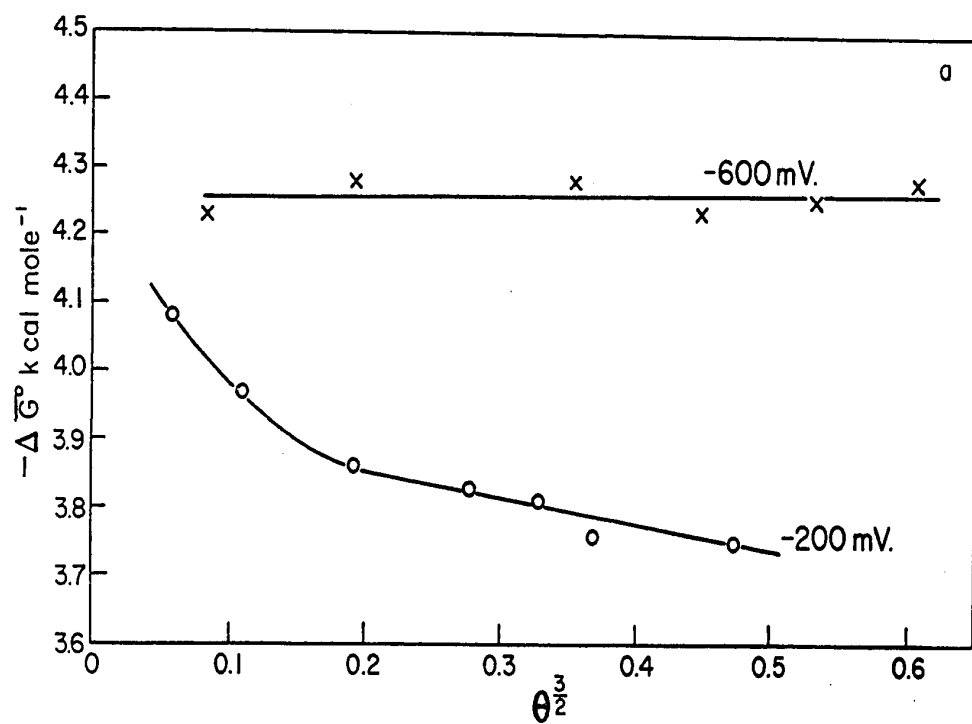


Figure XVIII:

- a. Plots of $\Delta \bar{G}^0$ vs $e^{3/2}$ for 2-aminopyridine in N KCl at various electrode potentials.
- b. Plots of $\Delta \bar{G}^0$ vs $e^{3/2}$ for aniline in N KCl at various electrode potentials. Solid line for $\Gamma_{\text{max.}} = 7.1 \times 10^{-10}$ mole cm^{-2} , dotted line for $\Gamma_{\text{max.}} = 8.8 \times 10^{-10}$ mole cm^{-2} .



Similarly, if it be assumed that aniline (Figure XVIII b) lies flat rather than normal to the surface, a single line for $\Delta \bar{G}^0$ vs $\theta^{3/2}$ (but with an increased slope) is still obtained e.g. at $E_{cal} = -400$ mv. The inflexions in the $\Delta \bar{G}^0 - \theta^{3/2}$ lines for the bases other than aniline are therefore quite real and would appear to be reasonably attributable to the onset of "cooperative" orientation of the film of dipoles as the surface coverage increases and as the films become more "condensed".¹⁷⁸

Evidence for this conclusion is given by the following facts:

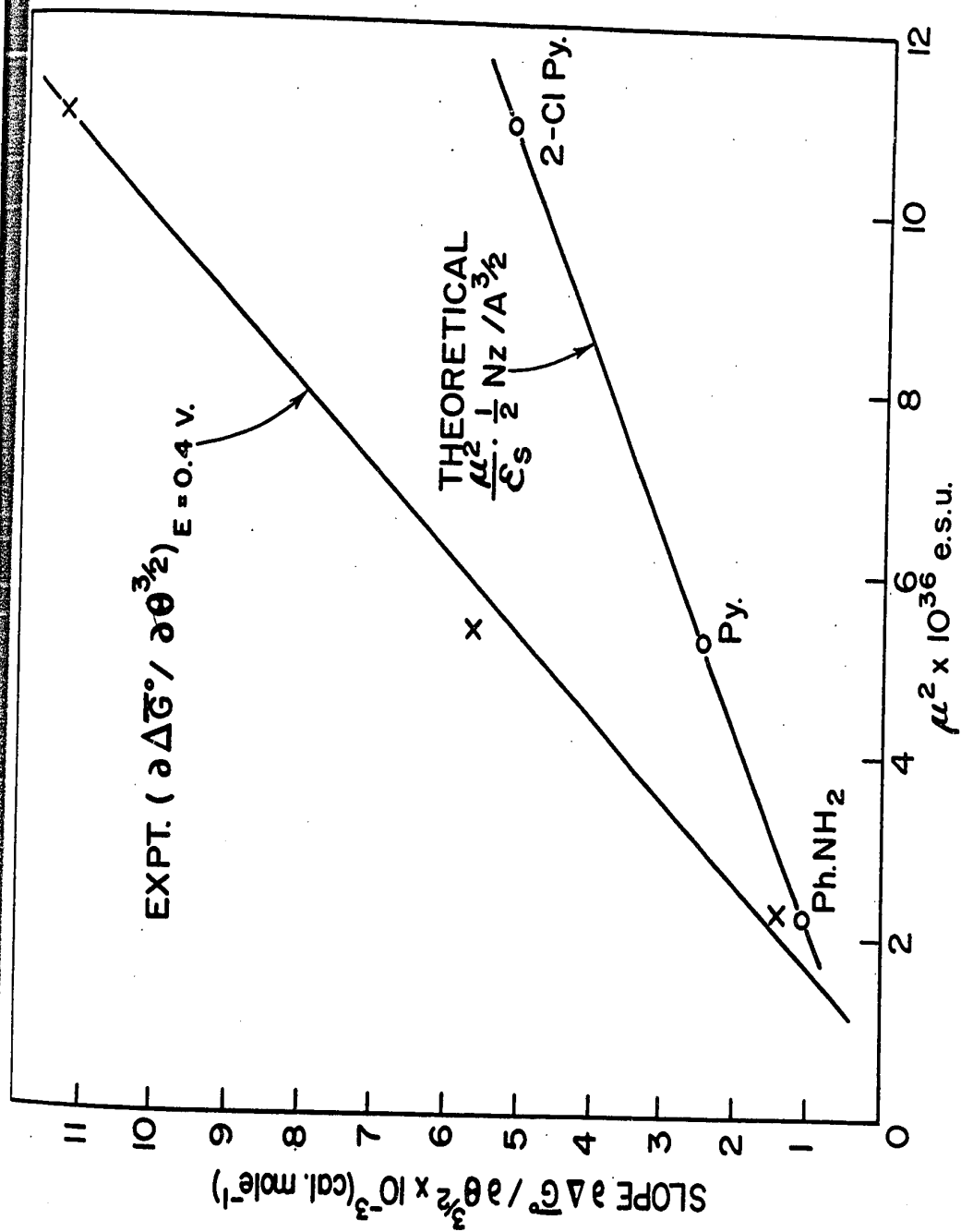
(1) The slopes of the $\Delta \bar{G}^0 - \theta^{3/2}$ lines increase with increasing field away from the c.c.m. potential corresponding to increasing orientation of the molecules by the field. The effective component of the dipole normal to the surface (i.e. in the direction leading to repulsion) would tend to increase with the electrode field so that the repulsion coefficient $\mu^2 / \epsilon_s \pi^{3/2} R^3$ of ϕ_{11} , and hence the slope of the $\Delta \bar{G}^0 - \theta^{3/2}$ lines would increase. Both parts of the inflected lines are seen to increase in slope as the electrode field increases (E_{cal} . decreasing numerically).

The fact that the inflexion in the $\Delta \bar{G}^0 - \theta^{3/2}$ lines occur at widely different critical values of θ (or $\theta^{3/2}$) for the different electrode potentials makes it unlikely that they arise from sudden changes of ϵ_s or water structure in

the surface layer. Such behaviour would only be expected as the mole fraction of water in the surface layer becomes small as $\theta \rightarrow 1$. However, there is apparently a relation between the surface concentration of adsorbate at which the inflexion occurs and the electrode field. At low fields near the e.c.m., an high θ must be reached before evidence of orientation can be seen and conversely, at high fields, the inflexion occurs at low θ . We may suggest that orientation sets in at a critical net total field determined by (a) the impressed electrode-solution potential difference and (b) the field of other dipoles in the surface layer. When the field due to (a) is low a high θ must be reached before the field associated with (b) is sufficient to cause a substantial degree of orientation, and vice versa.

(2) The slopes $(\partial \Delta \bar{U}^0 / \partial \theta^{3/2})_E$ of the steeper regions of these lines can be semi-quantitatively accounted for in terms of the dipole moment of the molecule and the dielectric constant of the surface layer assuming complete orientation in the surface layer. This is demonstrated in Figure XIX (page 151) where the experimental $\Delta \bar{U}^0 - \theta^{3/2}$ slopes are seen to be proportional to μ^2 and to be in order agreement with the theoretical slopes calculated using the ordinary dipole moment and $\epsilon_s = 1$. In a number of cases the apparent dipole moment relevant for molecules in a condensed surface film is found to

Figure XIX: Test of equation 118; Plot of slopes
 $(\partial \Delta \tilde{\epsilon}^0 / \partial e^{1/2})_R$ vs μ^2 .



be about twice the normal value¹⁷⁵⁻¹⁷⁷ and with the more reasonable value of $\epsilon_s \approx 2$ [i.e. $\epsilon_s \approx n^2$, the Maxwell value for a dielectrically saturated oriented film (cf. reference (31))] almost quantitative agreement between the experimental and theoretical slopes would be obtained.

(3) The variations of the change of e.c.m. potential $\Delta E_{\text{e.c.m.}}$, with $\log$ [concentration] of base and with $(\Gamma_A)_{\text{e.c.m.}}$ are shown in Figures XX and XXI (pages 153-154) respectively, from which it is seen that $d(\Delta E)_{\text{e.c.m.}}/d(\Gamma_A)_{\text{e.c.m.}}$ increases abruptly with increasing concentration or Γ_A . It is usually suggested^{150,179} that

$$\Delta E_{\text{e.c.m.}} = \frac{4\pi n \mu}{\epsilon_s} \cdot \Gamma_A \quad (126)$$

It appears that no thermodynamic basis has yet been given for this relation (as it has for the corresponding one for ion adsorption) and the validity of the R.H.S. as an expression for the surface potential difference of an adsorbed layer has been questioned.¹⁷² A thermodynamic relationship between $\Delta E_{\text{e.c.m.}}$ and concentration or Γ_A will be given in a later section of this thesis.

For oriented films the effective μ will be greater¹⁷⁵⁻¹⁷⁷ than for unoriented films and hence $\Delta E_{\text{e.c.m.}}$ would change more rapidly with Γ_A after orientation had set in. Such an effect is seen in Figures XX and XXI, which thus support the hypothesis of relatively sudden orientation; this behaviour is

Figure XX: Shifts of the potential of the electrocapillary maximum $\Delta E_{e.c.m.}$ with base concentration C in N KCl.

- | | |
|-----------------------------|---|
| $\square$ 2-chloropyridine; | $\circ$ Aniline; |
| Δ Pip-ridine; | Δ 1,2,3,6-Tetra-
hydropyridine; |
| $\times$ 2-Aminopyridine; | $\bullet$ Pyridine. |

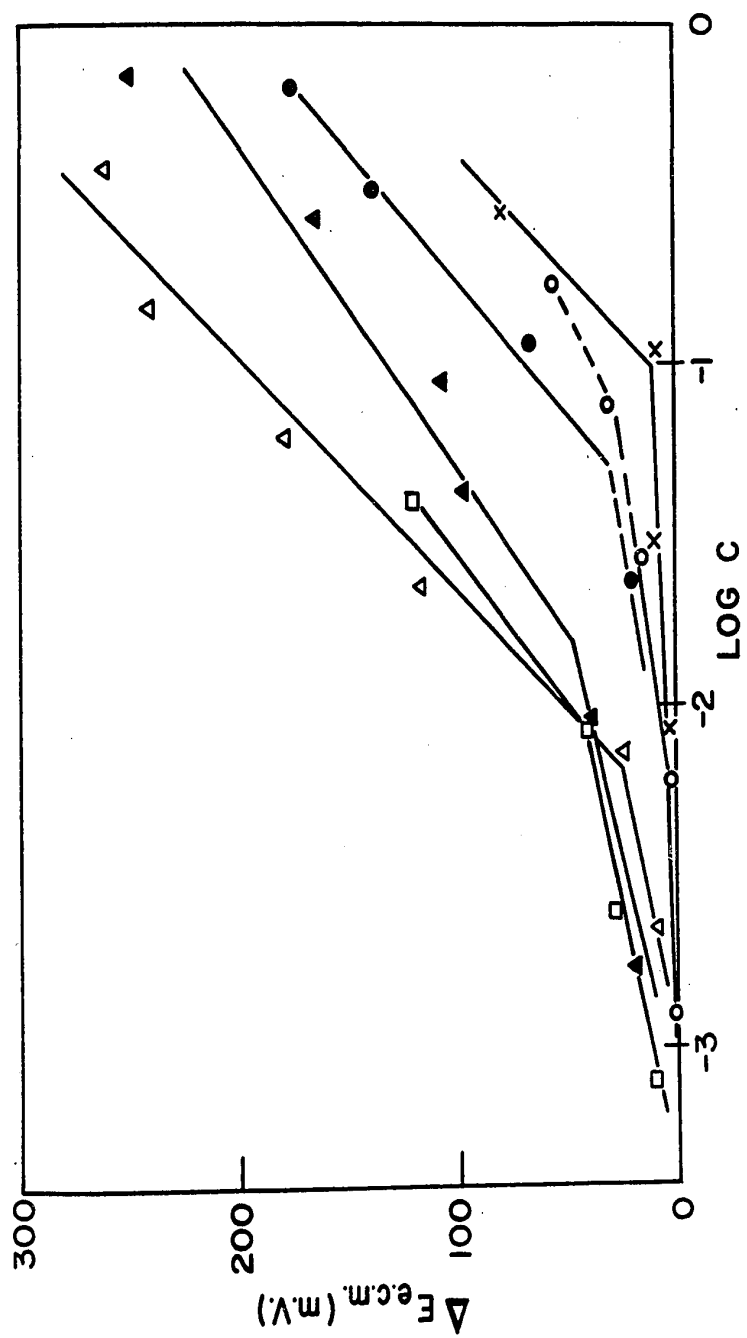
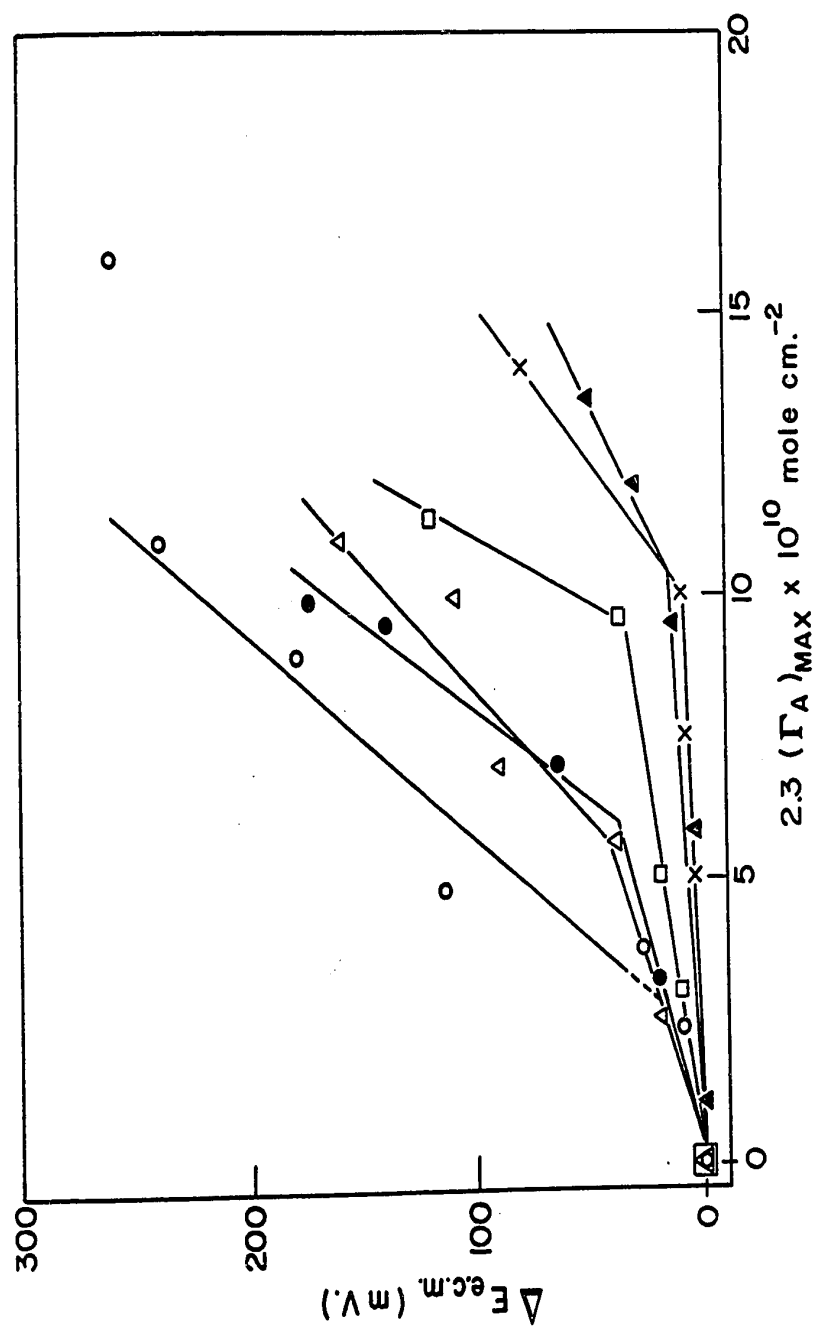


Figure XXI: Dependence of $\Delta E_{\text{e.c.m.}}$ upon $\sqrt{A}$ at the e.c.m. potential in N HCl

- | | |
|------------------------------------|--------------------|
| □ 2-Chloropyridine; | ○ Piperidine; |
| ● Pyridine; | × 2-Aminopyridine; |
| Δ 1,2,3,6-Tetra-
hydropyridine; | ▲ Aniline. |



also consistent with that found for the variation of $\Delta \bar{E}^0$ with coverage. It is to be noted that breaks are not observed in the corresponding plots of $\Delta E_{e.c.m.}$ vs $\log [\text{concentration}]$ for the organic molecules in their ionic form (cf. Section 8 of this Chapter) and this leads to further indirect, if negative, evidence for the hypothesis of orientation of the neutral molecules made here. It is likely that the $\Delta E_{e.c.m.}$ values and the slopes $(\partial \Delta \bar{E}^0 / \partial \theta^{3/2})_E$ are both connected with the π -orbital interactions with the metal. Those molecules such as aniline and 2-aminopyridine having the least " π -deficiency" will tend to be the most strongly adsorbed in the "flat" orientation through the π -orbitals: conversely, the more " π -deficient" pyridine and hydrogenated pyridine derivatives will have less (or no) specific π -orbital affinity for the mercury surface in the flat orientation and small fields or higher surface concentrations will more easily orient the dipolar molecules into the perpendicular position. Figure XX shows that the biggest shifts of the e.c.m. are caused by those molecules having least development of a conjugated π -orbital system. The observed $\Delta E_{e.c.m.}$ values are not directly related to the actual dipole moments of the molecules and this confirms that other chemical effects are modifying the moment effective in a direction normal to the surface through orientation effects. Similar effects are discerned in Figure XXI where $\Delta E_{e.c.m.}$ is plotted against the surface

excess of the base; a critical surface concentration is reached (corresponding to orientation discussed above) at which $\Delta E_{\text{e.c.m.}}$ suddenly increases, and the effect is apparently again related to the electronic structure of the molecule. Similar π -orbital effects are carried through to the conjugate acids (see Section B, this Chapter).

The anomalous behaviour (with regard to lack of inflexion in the $\Delta E^0 - e^{3/2}$ line) of aniline and to some extent of 2-aminopyridine could be accounted for as follows. In both of these molecules, the NH_2 -group could provide a component of moment normal to the electrode surface even if the phenyl ring were lying flat with maximum π -orbital interaction with the metal. In the interface, free rotation of NH_2 will tend to be inhibited by the proximity of the group to the metal surface and by hydrogen bonding with neighbouring solvent molecules as well as by any electrode field in the double layer. There can hence arise a component $\bar{\mu}$ of the $-\text{NH}_2$ group dipole (trigonometric vector calculation gives $\bar{\mu} = 1.25 \text{ D}$) normal to the surface which will lead to repulsive interactions with the corresponding components of other dipoles. Since we are suggesting that this repulsive effect can arise with aniline molecules already lying flat we shall not necessarily expect a change of slope of the $\Delta E^0 - e^{3/2}$ lines attributed to onset of increased orientation; none is in fact observed over

the range of concentrations examined (see Figure XVIII). This type of effect could not occur with unsubstituted N-heterocycles or in cases where the dipole moment of the substituent group is in the same plane as the ring and will thus not be observed in the cases of pyridine, 2-chloropyridine etc.

(vii) Some Aspects of the Adsorption of Multi-ring N-heterocyclic Compounds

Some studies of the adsorption at mercury of N-heterocyclic compounds such as pyridine, quinoline, acridine, benzaacridine etc., were attempted from N KCl solutions. The electrocapillary curves for pyridine have been shown in Chapter II; those for quinoline are given in Figure XXII a (page 158). The electrocapillary curves for acridine in N KCl solution are not reported because of the very limited range of concentrations over which Γ_A could be determined. This is due to the relatively low solubility of acridine (determined spectrophotometrically as 3.4×10^{-4} M as will be described in detail later). The solubilities of benzaacridines and dibenzaacridines are practically negligible ($< 10^{-5}$ M).

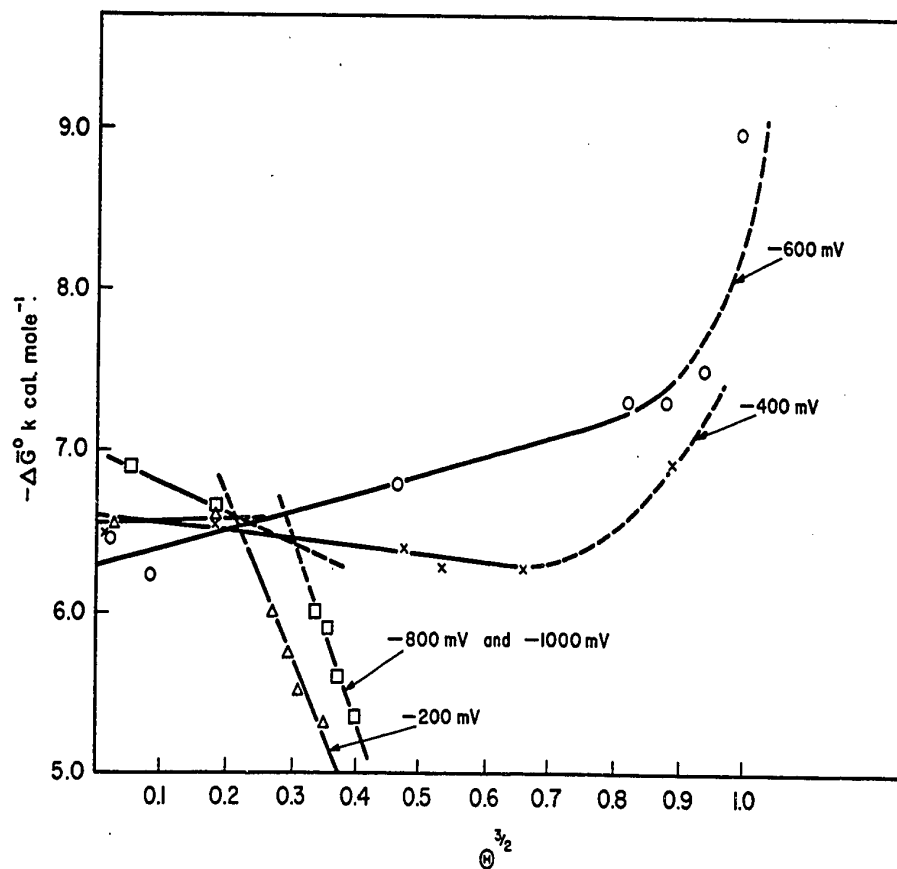
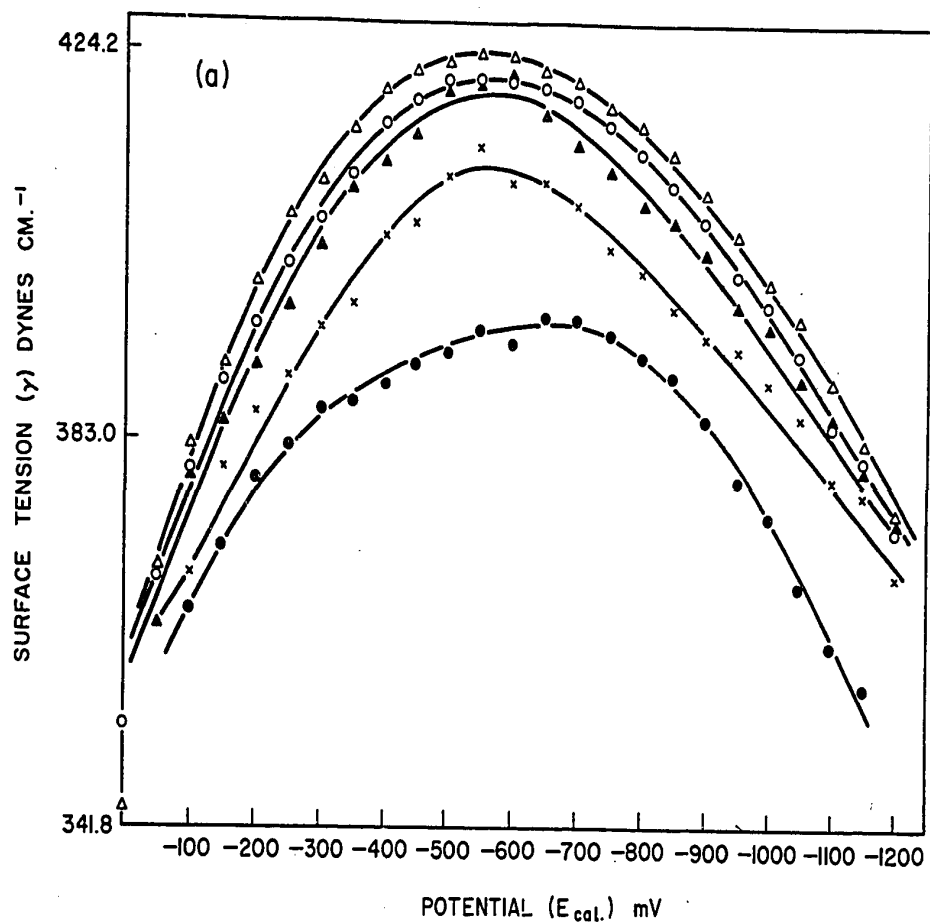
Despite the limitations of solubility, a small but noticeable depression of surface tension ($\Delta\gamma = 3 \text{ dynes cm}^{-1}$) was observed over a wide range of potentials for the adsorption of acridine on mercury from a solution whose concentration was only 10^{-6} M. When taken in comparison with the electrocapillary

Figure XXII:

(a) Electrocapillary curves for quinoline in
1 N KCl

Δ 1 N KCl; $\circ$ $8.06 \times 10^{-5} M$;
 Δ $4.03 \times 10^{-4} M$; $\times$ $2.02 \times 10^{-3} M$;
 $\bullet$ $8.06 \times 10^{-3} M$.

(b) Plot of $\Delta \bar{\epsilon}^0$ vs $\theta^{3/2}$ for quinoline in
1 N KCl at various electrode potentials.



behaviour of pyridine and quinoline, this result confirms the qualitative trend noted in the work on solid electrodes (Chapter V) that the degree of adsorption parallels the molecular size and solubility of the adsorbate. Figure VIII (a) shows only small values of $\Delta\chi$ for pyridine concentrations within the range 10^{-3} M to 10^{-2} M. Inspection of Figure XXXI indicates that quinoline begins to become significantly adsorbed by mercury at concentrations of about 10^{-5} to 10^{-4} M. Pyridine is infinitely soluble in water whereas quinoline is only moderately so, and by comparison acridine is the least soluble of the three compounds.

The adsorption of the conjugate ions of multi-ring N-heterocyclic bases could not be determined as the size of the molecule was increased beyond that of quinoline because at negative polarisations the large molecules, viz dibenzacridine, benzacridine, acridine and to some extent quinoline in acid media, showed a tendency to block the capillary. This may be interpreted as due to discharge of the organic ion at high negative potentials, which converts it to the neutral and less soluble molecule.

The experiments discussed here on multi-ring systems were not entirely fruitless, since the complete electrocapillary curves for a reasonable range of concentrations of quinoline in K potassium chloride solution were successfully obtained, and these results have been used to determine the nature of

the orientation of quinoline at the mercury surface by examining the $\Delta \bar{G}^0 - \theta^{3/2}$ plots at various potentials (see Figure XXII b) as described previously. The curves in Figure XXII b are for the most part linear and there are again inflections at high concentrations and at high positive or negative fields. At potentials near the e.c.m. $\Delta \bar{G}^0$ appears to be the least dependent on $\theta^{3/2}$. This may be due to flat orientation through π -orbital interaction with mercury (cf. Figure XVII b for pyridine at -600 mV.); this effect persists up to rather high values of surface coverage ($\theta^{3/2} = 0.7$). At high values of $\theta^{3/2}$, the curves for potentials near that of the e.c.m. deviate markedly from linearity but this effect is quite consistent with that expected from the operation of Van der Waals attractive forces at higher coverages (cf. page 155). In general, it would appear that the results for quinoline support the previous treatment given for single ring π -heterocyclic bases.

(viii) Surface Charge in the Presence of the Neutral Bases

The surface charge on the metal q_M is obtained from the Gibbs-Lippmann equation as

$$-q_M = (\partial \gamma / \partial E)_{\mu_{KCl}, \mu_A} \quad (127)$$

Values of q_M for four of the bases at various concentrations and electrode potentials are shown in Figures XXIII (page 161). In all cases q_M is numerically decreased with increasing base

Figure XXIII:

Charges upon the metal surface as a function of electrode potential and base concentration

(a) Pyridine in N KCl

○ 1 N KCl;	x 2.35×10^{-2} M;
□ 1.18×10^{-1} M;	Δ 3.15×10^{-1} M;
● 6.29×10^{-1} M.	

(b) Piperidine in N KCl

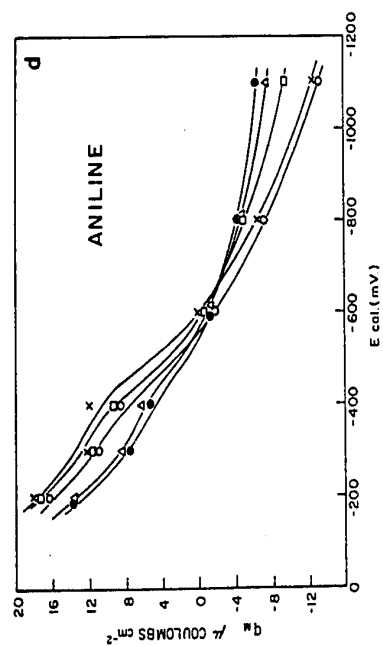
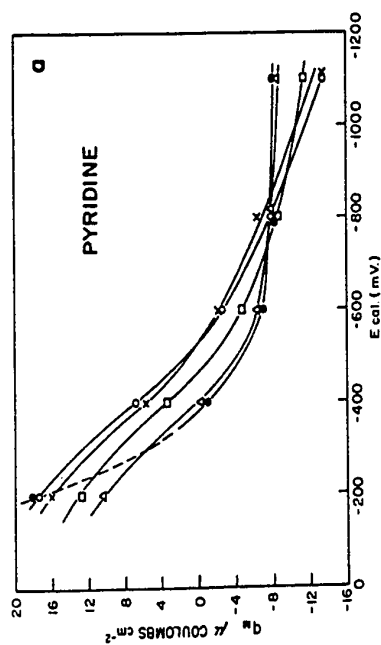
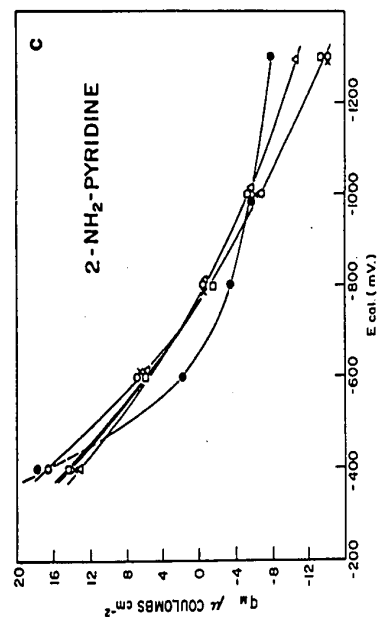
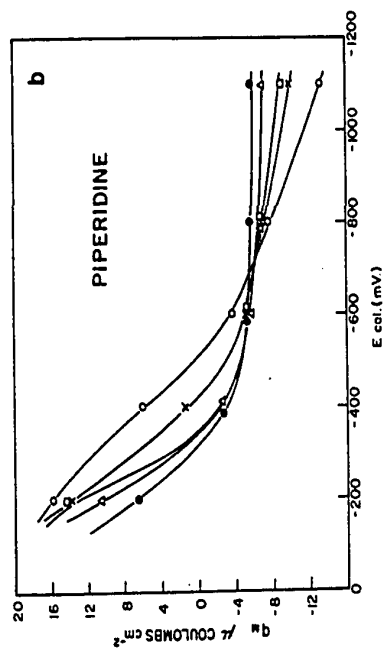
○ 1 N KCl;	x 2.27×10^{-2} M;
□ 6.12×10^{-2} M;	Δ 1.50×10^{-1} M;
● 3.98×10^{-1} M.	

(c) 2-Aminopyridine in N KCl

○ 1 N KCl;	x 8.72×10^{-3} M;
□ 3.05×10^{-2} M;	Δ 1.17×10^{-1} M;
● 2.92×10^{-1} M.	

(d) Aniline in N KCl

○ 1 N KCl;	x 6.10×10^{-3} M;
□ 2.70×10^{-2} M;	Δ 7.85×10^{-2} M;
● 1.70×10^{-1} M.	



ADSORPTION AT ELECTRIFIED INTERFACES

by

Remigio Germano Barradas

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concentration and at potentials cathodic to the e.c.m. becomes almost independent of potential. The effects are less with the least π -deficient molecules 2-aminopyridine and aniline, and this is probably connected with their "flatter" orientation (discussed above) at the interface with correspondingly smaller net induced dipole charge at the metal surface due to a smaller degree of "perpendicular" orientation of the dipoles.

(ix) Relationship to Sorption at the Air-water Interface

It is of interest to examine if the electrochemical free energy of adsorption of the bases at mercury (at the potential of the e.c.m.) is comparable with that for adsorption of the same molecules at the air-water interface. Few data exist on which a suitable comparison can be based; however, surface tension measurements have been reported for aniline and p-toluidine solutions in water^{180,181} and the appropriate Γ values and isotherms may be calculated from these data.

Using equation (108) for $\theta = 0.5$ we may compute the values of $\Delta \bar{G}^{\circ}$ shown in Table VII.

TABLE VII

Values of $\Delta \bar{G}^{\circ}$ at the e.c.m. at Hg and $\Delta \bar{G}^{\circ}$ for the air/water interface

Substance	$\Delta \bar{G}^{\circ}_{\text{Hg, e.c.m.}}$ (kcal.mole ⁻¹)	$\Delta \bar{G}^{\circ}_{\text{air/water}}$ (kcal.mole ⁻¹)
Aniline	-4.5 (1)	-3.8 (6)
p-Toluidine	-	-4.6 (4)

The difference between $\Delta \bar{G}^0$ and ΔG^{0*} for aniline at the Hg/water and air/water interfaces is probably significant and reflects a small extra specific adsorption energy at the e.c.m. due to interaction with the metal. It is clear that no large chemisorption energy of interaction with the metal is involved, and that most of the apparent $\Delta \bar{G}^0$ is determined by "escape" of the solute from the bulk solvent to its interface. The energy arising from specific interaction with the metal may be estimated in the case of aniline as the difference between the $\Delta \bar{G}^0$ and ΔG^0 values for the Hg/water and air/water interfaces, respectively, i.e. $-0.7 \text{ kcal.mole}^{-1}$ (no data are available at Hg for p-toluidine). The π -orbital interaction energies calculated in Section B of this Chapter may be seen to represent about 30-50% of that part of the free energy of adsorption associated with specific interaction of the organic molecule with the metal and, although small, are in this respect relatively quite significant.

B. COMPARISON OF ADSORPTION OF THE BASES AND THEIR IONS AT MERCURY

(i) Preliminary Remarks

In the present part of this work the aim has been to compare the adsorption of some neutral organic bases with that of their corresponding ions and to investigate the nature of the intermolecular forces leading to their adsorption at the

* The symbols $\Delta \bar{G}^0$ and ΔG^0 are used here to distinguish the the standard free energy of adsorption at the electrode in the presence of a field (cf. p. 138) from the standard free energy of adsorption at the air-water interface where no impressed field is involved.

The difference between $\Delta \bar{G}^{\circ}$ and $\Delta G^{\circ*}$ for aniline at the Hg/water and air/water interfaces is probably significant and reflects a small extra specific adsorption energy at the e.c.m. due to interaction with the metal. It is clear that no large chemisorption energy of interaction with the metal is involved, and that most of the apparent $\Delta \bar{G}^{\circ}$ is determined by "escape" of the solute from the bulk solvent to its interface. The energy arising from specific interaction with the metal may be estimated in the case of aniline as the difference between the $\Delta \bar{G}^{\circ}$ and ΔG° values for the Hg/water and air/water interfaces, respectively, i.e. $-0.7 \text{ kcal.mole}^{-1}$ (no data are available at Hg for p-toluidine). The π -orbital interaction energies calculated in Section B of this Chapter may be seen to represent about 30-50% of that part of the free energy of adsorption associated with specific interaction of the organic molecule with the metal and, although small, are in this respect relatively quite significant.

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mercury-solution interface. It is at once clear that such forces will be complex (cf. Appendix, this thesis), and the following factors will influence the adsorption of the ions and molecules: firstly the adsorbate-surface interaction energy will depend on both electrostatic and non-electrostatic effects. In the former class we include the interaction of adsorbed ions with the electrode field, of dipoles with the field and polarisation energy of the molecule or ion in the field; in the latter class we include the Van der Waals interaction with the surface, specific π -orbital interaction¹⁸²⁻¹⁸⁴ and any solvent "structure-breaking effects",¹⁸⁵⁻¹⁸⁶ which, being different for the adsorbate molecule at the interface compared with the situation in the solution, will contribute to the apparent energy of adsorption. There will also be included in the apparent adsorption energy, the energy involved in displacing adsorbed water molecules and this is related to the local "structure-breaking" and dielectric saturation effects in the region of solvent adjacent to the interface.

(11) Form of the Electrocapillary Curves in Acid Solutions

In acid solutions of all the bases, the electrocapillary curves are more symmetrical than in corresponding neutral solutions (see Chapter III). However, with all solutes except aniline and 2-aminopyridine there is little adsorption on the positive branch at potentials more positive than -250 mV

with respect to the calomel electrode in N HCl. The curves for aniline and 2-aminopyridine in the N HCl solution show an unexpected degree of symmetry since, being surface active cations, these adsorbates would be expected to be predominantly adsorbed only on the negative branch. The behaviour observed here is thus analogous to that found with the neutral solutions of these compounds, and will be discussed below.

(iii) Standard Electrochemical Free Energies of Adsorption

The variation of the extent of adsorption with electrode potential can best be expressed in terms of the variation of the standard electrochemical free energy of adsorption $\Delta \bar{G}^0$ of the adsorbates at a given surface coverage θ , e.g. $\theta = 0.25$ or $\theta = 0.50$, with electrode potential. We can obtain the Langmuir isotherm [equation (108)] in the form

$$\frac{\theta}{1 - \theta} = \frac{C_A}{55.5} e^{-\Delta \bar{G}^0/RT} \quad (128)$$

where all the terms have their usual significance as defined previously. If interaction effects are present $\Delta \bar{G}^0$ will be, as before, a function of surface coverage (alternatively, we could introduce f_θ as in equation (118)). $\Delta \bar{G}^0$ values are shown as a function of electrode potential in Figures XXIV and XXV (pages 166-167) for the various organic ions in 1.0 N

Figure XXIV: Values of the changes of standard electrochemical free energy $\Delta \bar{G}^{\circ}$ for the conjugate acid ions of the bases in 1 N HCl at various electrode potentials and at $\theta = 0.5$.

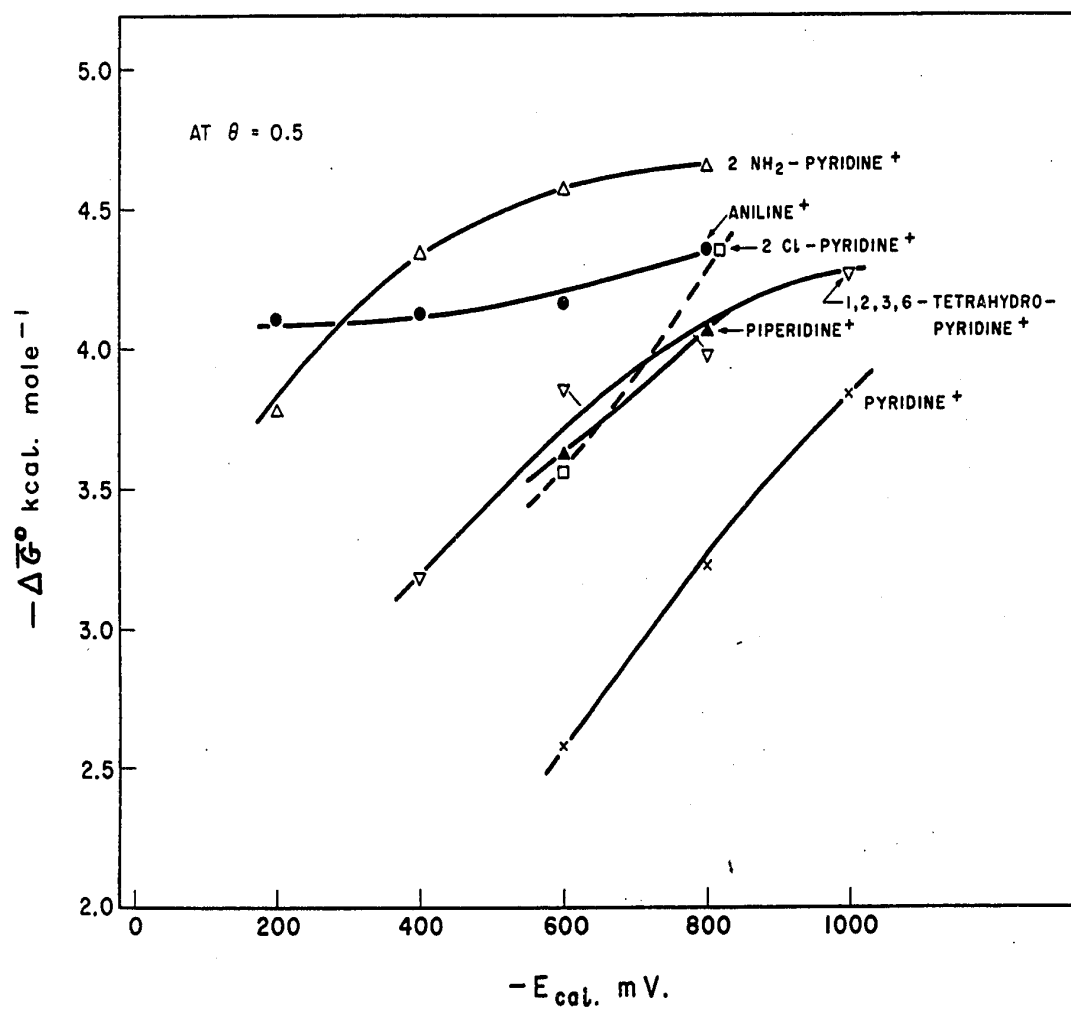
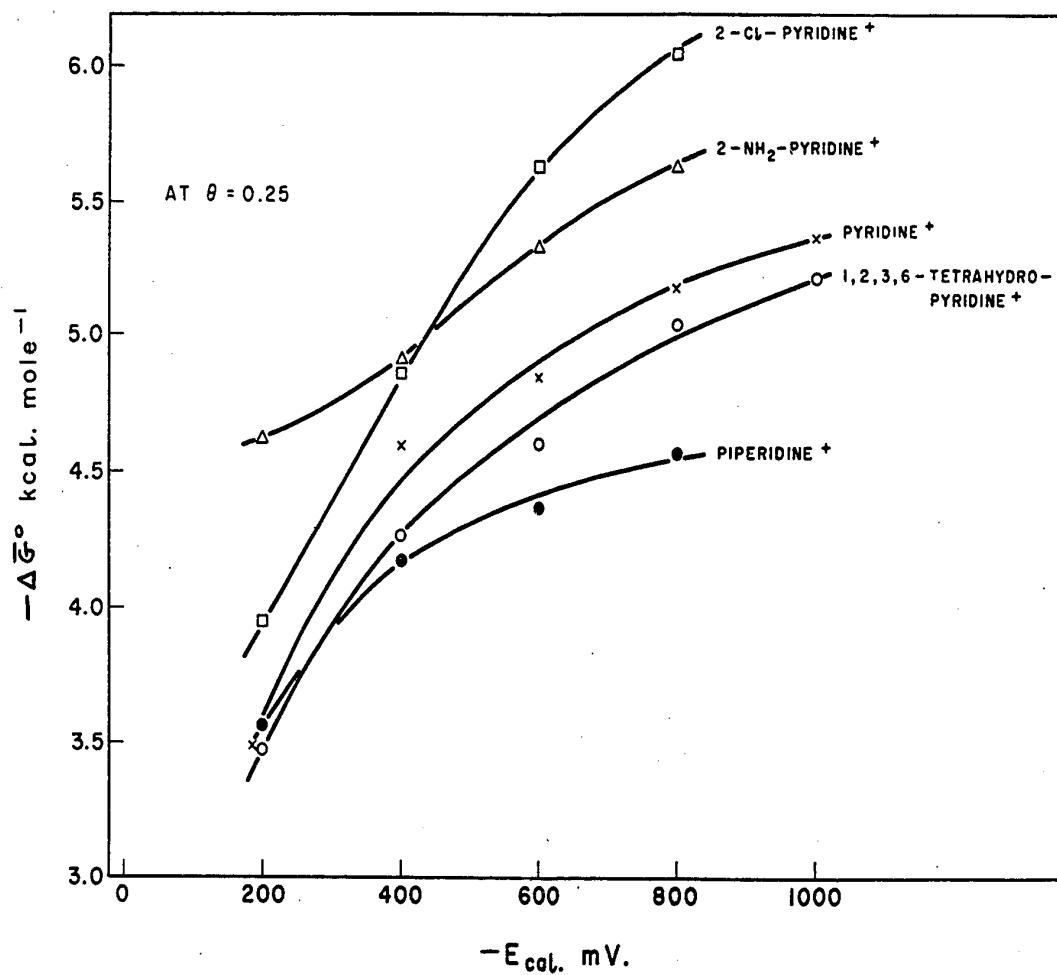


Figure XXV: Values of $\Delta \bar{G}^{\circ}$ for the conjugate acid
ions in 1 N HCl at $\theta = 0.25$.

Figure XXV: Values of $\Delta \bar{G}^{\circ}$ for the conjugate acid
ions in 1 N HCl at $\theta = 0.25$.



aqueous hydrochloric acid at $\theta = 0.25$ and 0.5 . It is evident that there is a more or less continuous increase of $-\Delta \bar{G}^{\circ}$ with increasing (negative) potential. For the adsorption of the aminium ions this is as expected since the organic cations are the surface active species and the chloride ion concentration is constant in these experiments. Values of $\Delta \bar{G}^{\circ}$ for $\theta = 0.5$ are less than those for $\theta = 0.25$ owing to repulsive ionic interaction effects in the surface layer to be discussed in more detail below. We may note that $\Delta \bar{G}^{\circ}$ is still quite negative even at the most positive polarisations (e.g. $E_{cal} = +200$ mV) so that there are appreciable specific ion-surface interaction forces as also indicated by the strong adsorption at the potential of the e.c.m. These specific effects on the anodic branch are greatest for anilinium and 2-aminopyridinium ions (Figure XXIV) and least for pyridinium ions. For the corresponding neutral molecules (Figure XVI) the same trend is observed; there is also a marked asymmetry in the $\Delta \bar{G}^{\circ}$ curves with respect to the potential of the e.c.m. The reasons for this may be as follows: (a) the organic bases are more easily oriented with their electronegative centres (N) outward towards the solution, as suggested by Gierst et al.,⁸⁶ where they can interact maximally with the solvent by hydrogen bonding and hence can be more satisfactorily hydrated on the cathodic branch than on the anodic where, upon being reoriented towards the positive mercury surface, they suffer less

favourable interaction with the solvent with a consequent diminution of the free energy of adsorption; and (b) on the anodic branch, specific adsorption of the chloride ion in the supporting electrolyte could diminish the adsorption of the organic solute by a surface "salting-out" effect. Factor (a) is probably of greatest importance since with thiourea, whose hydrophilic end of the molecule is composed of the electro-positive NH_2 groups, the strongest adsorption is found now on the anodic^{83,84,150} rather than the cathodic branch. The standard electrochemical free energies of adsorption of the neutral bases and their corresponding conjugate acids are compared in Table VIII (page 170) from which it is seen that the ions are usually less strongly adsorbed than the corresponding neutral bases. The smallest difference, and one case of reversal, arises with aniline and 2-aminopyridine, respectively, molecules for which there are reasons to expect somewhat stronger adsorption in the ionic form owing to resonance effects (see below). Apart from the case of 2-aminopyridine, the general trend is as expected since the ionic group will prefer not to reside in the interface since at such a location its electrostatic sphere of influence (Born solvation) in the solvent will be restricted.

It has been shown in the foregoing discussion that the principal contribution to the electrochemical free

TABLE VIII

Comparison of Free Energies of Adsorption of the Bases in
Neutral and Ionic Forms

Adsorbate	At $E_{\text{cal.}} = -600$ mV.		At $E_{\text{cal.}} = -600$ mV.	
	$-\Delta \bar{G}$ (Ionic) kcal.mole ⁻¹		$-\Delta \bar{G}$ (Neutral) kcal.mole ⁻¹	
	$\theta = 0.5$	$\theta = 0.25$	$\theta = 0.5$	$\theta = 0.25$
Pyridine	2.5 (8)	4.8 (3)	3.3 (5)	-
2-NH ₂ -pyridine	4.5 (6)	5.3 (3)	4.0 (5)	-
2-Cl-pyridine	3.5 (5)	5.6 (2)	5.3 (6)	5.9 (5)
1,2,3,6-tetra- hydropyridine	3.7 (0)	4.6 (1)	4.5 (5)	-
Piperidine	3.6 (2)	4.3 (8)	4.6 (0)	-
Aniline	4.1 (8)	-	4.5 (2)	-
Mean difference at $\theta = 0.5$	0.69			

Notes: The errors in these $\Delta \bar{G}$ values and elsewhere in the
Figures may be estimated as follows. The errors in
values arising from errors in $(\partial \delta / \partial \mu_A) E, \mu_{\text{HCl}}$ vary

from 0.5 to about 1% with increasing negative potential
corresponding to errors in γ and any uncertainties about the
activity coefficients of the organic ions. The Γ values at each
potential are converted to θ values by assuming a certain value
of Γ_{max} for $\theta = 1$ based on the projected area of the ions or
molecules lying flat or perpendicular to the surface. In the
case of the ions, the observed Γ_{max} corresponds to ions lying
"flat" upon the surface whilst for the neutral molecules Γ_{max}
corresponds (when ϕ_r is 0 or negative) to more oriented dipoles
as $\theta \rightarrow 1$. When $\theta < 1$, calculations of θ from $\Gamma / \Gamma_{\text{max}}$ are
thus uncertain in so far as the Γ_{max} values are based on

TABLE VIII - Continued

(Notes - continued from page 170).

molecular areas obtained from space-filling (Courtauld) models. The areas thus deduced are probably correct to within $\pm 2 \text{ \AA}^2$ in $20 \text{ \AA}^2$ or to 10%. $\Delta \bar{G}^0$ is calculated however from $\log \frac{\theta}{1-\theta}$ and the probable error in $\theta/1-\theta$ will be about 10% and the maximum error 20%, giving an error in $\log (\theta/1-\theta)$ at ($\theta = 0.5$ for example) of ± 0.08 . The error in $\Delta \bar{G}^0$ will hence be $\pm RT 0.08$, i.e. $\pm 0.05 \text{ kcal. mole}^{-1}$ assuming no significant errors in solution concentrations or temperatures. The differences of $\Delta \bar{G}^0$ recorded in Table VII for ionic and neutral species are therefore entirely significant.

energy of adsorption of the bases in neutral form arises from the tendency of the organic residue to escape from the polar water phase to the metal interface, this effect being quantitatively similar to that occurring at the air/water interface. As in the case of ionic detergent molecules (e.g. fatty acid salts), the organic residue in an organic ion will similarly tend to reside preferentially at the interface even though the ionic centre tends to remain in the aqueous phase. Provided that geometrical factors allow the latter condition to be realised, the electrochemical free energies of adsorption of a molecule in neutral and ionic forms should, to a first approximation, only differ by any changes of free energy of solvation of the ionic form brought about by the presence of the charge centre near (but not in) the interface.

Payens¹⁸⁶ has calculated the free energy ΔG_H of "partial dehydration" as an ion (in water) becomes adsorbed at an oil-water interface as

$$\Delta G_H = + 3 e^2 / 4 \epsilon d \quad (129)$$

where ϵ is the bulk dielectric constant of water and d the distance of the adsorbed ion from the surface. Using the same method of calculation (q.v.¹⁸⁶) we may modify Payens calculation to make it applicable to the mercury-water interface. Taking the dielectric constant of the metal as effectively "infinite" we now obtain as a lower limiting value

$$\Delta G_H = + e^2 / 4d\epsilon \quad (130)$$

With $\epsilon = 78$ and $d \doteq 4 \text{ \AA}$ (the approximate radius of the primary hydration layer at the charge centre of the monovalent organic ion in the (outer) Helmholtz layer) $\Delta G_H \doteq 0.25 \text{ kcal. mole}^{-1}$, a figure having the same order of magnitude as the mean difference of electrochemical free energy of adsorption of the neutral bases and their ions given in Table VIII. From these data and the calculated value of ΔG_H it is clear that (a) the presence or absence of an ionised centre in the molecule makes very little difference to $\Delta \bar{G}^0$ for otherwise similar molecular and electronic structures; (b) that adsorption of the organic ion involves only small changes in "secondary" and not "primary" hydration¹⁹ and (c) the condition of

the ion (from a solvation point of view) at the interface is, as a consequence, very similar to that of the ion in solution. An interesting corollary to these conclusions is that solubility is not always an important factor in determining strength of adsorption in solution systems, since the bases and their ions have, in most cases, quite different solubilities.

(iv) π -Orbital Interaction with the Metal Surface

Previous studies with conjugated unsaturated hydrocarbons and their hydrogenated derivatives¹⁸²⁻¹⁸⁴ have shown that adsorption on the positive branch is stronger when unsaturation is present in the molecule although the extent of adsorption of saturated and unsaturated analogues is approximately the same on the negative branch. The suggestion was therefore made that these effects were due to specific π -orbital interaction with ^{the} "electron-deficient" mercury surface at potentials anodic to the e.c.m.* It was noted previously that aniline and 2-aminopyridine are more strongly adsorbed than pyridine (and also 2-chloropyridine) at anodic potentials and that the same effects occur, as discussed above, with the corresponding ions. It therefore appears that π -orbital interaction with the positive mercury surface is

* A similar suggestion was made with regard to adsorption of N-heterocyclic bases at solid electrodes.^{187,188}

one of the factors determining the free energy of adsorption of these compounds and their ions. From Gerowicz' work,¹⁸²⁻¹⁸⁴ it is possible to estimate the contribution to $\Delta \bar{G}^{\circ}$ from π -orbital effects by calculation of the difference $\Delta \Delta \bar{G}^{\circ}$ of $\Delta \bar{G}^{\circ}$ values at a given anodic potential for saturated and unsaturated analogues, e.g. naphthalene and decalin. This calculation is carried out as follows. We first obtain an estimate[†] of $d\gamma/d\mu$ at a given electrode potential for the hydrocarbons from the published electrocapillary curves by assuming that a significant depression of γ occurs first at about 10^{-4} M for single aromatic ring systems, 10^{-5} M for double and at 10^{-6} M for fused triple ring systems (this is based on the findings given on pages 157-8, for the corresponding neutral N-heterocyclic bases; the calculated values of $\Delta \Delta \bar{G}^{\circ}$ can be shown to be relatively insensitive to the values assumed for this limiting concentration). The values of Γ for the hydrocarbons thus obtained from the mean derivative $\Delta\gamma/\Delta\mu$ are then converted to the corresponding surface coverages and the $\Delta \Delta \bar{G}^{\circ}$ calculated from equation (128) from which it will be apparent that

$$\frac{\Delta \Delta \bar{G}^{\circ}}{RT} = 2.3 \log \left[\frac{\theta_1}{1 - \theta_1} \cdot \frac{1 - \theta_2}{\theta_2} \right] \quad (131)$$

[†] An exact calculation of this quantity is not possible since an insufficient range of concentrations were studied in the original published work.

where θ_1 and θ_2 are the surface coverages at a given electrode potential for two hydrocarbons 1 and 2 with the same number of 6-membered rings but differing only in degree of unsaturation. $\Delta \bar{G}^\circ$ values are summarised in Table IX (page 176) from which it is seen that $\Delta \bar{G}^\circ$ tends to increase with increasing anodic electrode potential. It must be borne in mind, however, that hydrogenation of the conjugated systems will also modify the interaction with the solvent since the π -orbitals in conjugated aromatic rings can specifically hydrogen-bond with OH-functions^{189,190} as in the methanol used as solvent in this work, so that $\Delta \bar{G}^\circ$ reflects not only differences of interaction of the hydrocarbon with the metallic surface but with the solvent as well. The largest apparent π -orbital effects are at the most positive potentials (with respect to the e.c.m.), thus indicating that an electron deficient mercury surface is necessary for the effect to be manifested. It is of interest that hydrocarbon π -orbital complexes are well known e.g. those of ethylene with Pt (II) and Pt (III) and other transition and neighbouring metals e.g. Ag (I), Hg (II),^{191,192} similarly, with quaternary heterocyclic ions e.g. methylpyridinium (+), an analogous π -complex bearing a delocalised charge has been reported.¹⁹³ Adsorption of both conjugated ions and corresponding neutral molecules at the positive mercury surface through π -orbital interaction is thus not inconsistent

TABLE IX

Hydrocarbon pair	$\Delta \Delta \bar{G}^{\circ}$ mole ⁻¹ kcal.	$E_{cal.}$ Volts	Δn
Benzene-cyclohexane	0.44	- 0.2	3
Naphthalene-decalin*	0.51	- 0.1	5
	0.28	- 0.2	
	0.17	- 0.3	
Anthracene-tetra hydroanthracene	0.42	- 0.1	2
	0.37	- 0.2	
Anthracene-octahydro anthracene	0.32	- 0.1	4
	0.26	- 0.2	
Mean $\Delta \Delta \bar{G}^{\circ} / \Delta n$	0.13	- 0.1	1
	0.11	- 0.2	

* Isomeric form not stated in original paper.

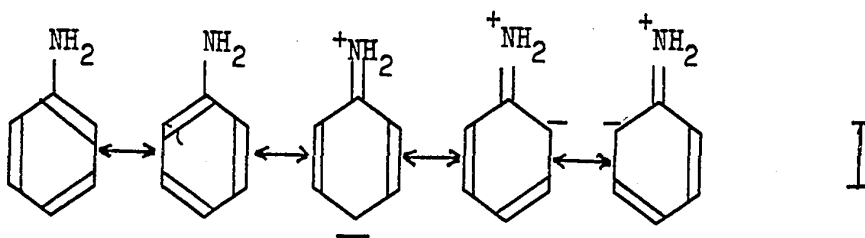
Δn is the difference of the number of conjugated double bonds between the respective pairs of hydrocarbons compared.

with the known chemistry of analogous stoichiometric complexes.

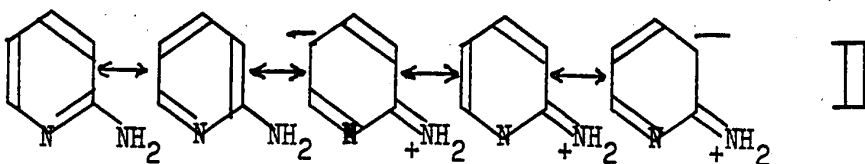
However, with regard to the heterocyclic bases studied in the present work, the values of $\Delta \bar{G}^{\circ}$ are only about 10 percent of the total electrochemical free energies of adsorption, so that the π -orbital effects are not so striking in these heterocyclic systems as with hydrocarbon systems, presumably because of stronger polar effects and greater specific interaction (through hydrogen bonding and "structure breaking" effects) with the solvent in the former cases. Thus, it has already been shown in Section A (IX) of this Chapter that the values of $\Delta \bar{G}^{\circ}$ at the s.c.m. at mercury are not greatly different from the corresponding quantity for adsorption at the air/water interface.

The electrocapillary curves for aniline and 2-amino pyridine, both as ions and neutral molecules, show an unusual and perhaps unexpected degree of symmetry except at the highest concentrations, and the corresponding plots of $\Delta \bar{G}^{\circ}$ with respect to electrode potential show the least variation of $\Delta \bar{G}^{\circ}$ compared with that, for example, found for pyridine or 2-chloro-pyridine. It is evident that in these cases the π -orbital effects can be quite significant and be carried through from the neutral molecules to the corresponding ions. This behaviour can be related to the resonance in aniline and 2-aminopyridine; when neutral, these molecules can be represented by the

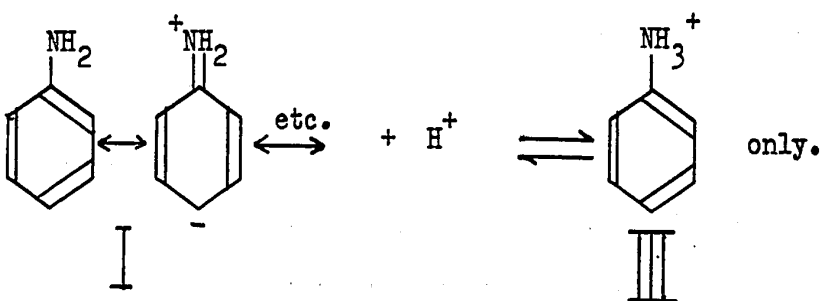
canonical forms:



and



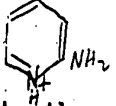
Upon ionisation



Upon ionisation in acid, I is completely converted to the "aromatic"* form III since the positive charge can then only reside on the amine N atom and no further unshared electron

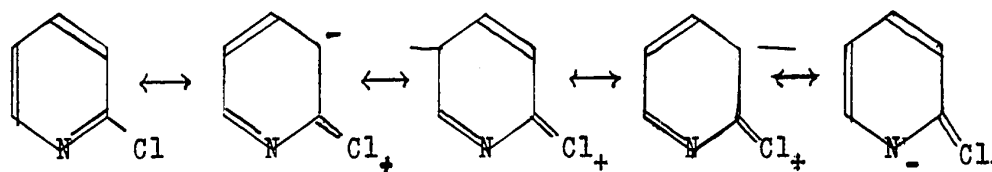
*

The term "aromatic" is used here in a general sense to refer to the type of resonating system in benzene (cf. the usage by Albert, ref. (165) p. 243).

pair is then available. Striking proof of this is afforded by comparison of the u.v. spectrum of I and its ion III where the spectrum of the latter is completely changed¹⁶⁵ and resembles that of benzene. Similarly, for II, ionisation in dilute acid converts the molecule to  (IV), where the proton is almost exclusively bonded to the ring nitrogen atom. We thus see that despite the positive charges on III and IV, they can in fact have as much "aromatic" character* as the corresponding neutral molecules, and we suggest that this may be connected with their strong adsorption on the positive as well as on the negative branch of the electrocapillary curve. Albert¹⁶⁵ has recently made a useful classification of heterocyclic substances into those which are " π -deficient" and those which are " π -excessive". In the first class are included the types of ring system studied here where the electronegative N atom in a six-membered ring "withdraws" electrons from the three double bonds (hence the term " π -deficient"); in the second, are heterocycles of the pyrrole kind. In the first class, modifications of the π -deficiency can be brought about by the introduction of substituents; thus, in the case of 2-aminopyridine, the presence of the electron "releasing" group

* Here again this term is used in the sense discussed on the previous page.

NH_2 makes the molecule much less π -deficient than pyridine¹⁶⁵ and the adsorption of the former substance indeed more closely resembles that of the aromatic molecule aniline than that of pyridine. Similarly, 2-chloropyridine is more π -deficient owing to the electronegative substituent and is less strongly adsorbed (Figure XVI) than 2-aminopyridine at positive potentials. However, its higher dipole moment than that of 2-aminopyridine leads to a higher electrostatic contribution to ΔG° at high fields and this tends to reverse the effect of the enhanced π -deficiency (arising from the Cl substituent) on the adsorption of this molecule. Also, mesomeric effects arising from resonance between



can give effects analogous to those in 2-aminopyridine since the Cl substituent has unshared pairs of electrons.

(v) Interaction between Adsorbed Ions

Surface equations of state for adsorbed ions at the mercury electrode have been discussed by Parsons^{36,29} and a more specific theory of ionic interaction effects on a surface leading to deviations from the Langmuir isotherm has also

already been given.³⁰ However, we shall examine some of the experimental isotherms obtained in Section A in the light of the previously published theoretical treatments and investigate the dependence of $\Delta \bar{G}^o$ for the adsorbate molecules in their ionic forms upon surface coverage θ .

By analogy with the treatment for dipoles given in Section A and that for ions elsewhere,³⁰ we may write the interaction potential ϕ_{11} per pair of ions on the surface at a mean distance of separation r as

$$\phi_{11} = \frac{e^2}{\epsilon_s r} - \frac{B}{\epsilon_o r^6} \quad (132)$$

where B is the Van der Waals - London coefficient. Assuming the coordination number n in the surface layer of ions to be six,¹⁹¹ the electrostatic interaction energy E_{11} for an assembly of N (Avogadro's number) ions is

$$E_{11} = \frac{1}{2} N n \phi_{11} = \frac{1}{2} N n \left[\frac{e^2}{\epsilon_s r} - \frac{B}{\epsilon_o r^6} \right] \text{ per mole} \quad (133)$$

With $\frac{1}{r} = \left(\frac{\theta}{A} \right)^{1/2}$ where A is the projected area of an adsorbed ion at the coverage θ , we find as shown previously^{30*} that E_{11}

* The actual result given here [equation (133)] differs from that previously deduced by Bockris and Blomgren³⁰ by the factor $1/2 n$ [cf. reference (192)] which must be included to allow for interactions amongst all nearest neighbours in the surface. Their equations give E_{11} too small by a factor of 3 if n is taken as 6.

and hence $\Delta \bar{G}^0$ decreases with the square root of θ at low values of θ (i.e. $\theta^{1/2} < \text{ca. } 0.75$). At high values of θ (i.e. $\theta^{1/2} > 0.75$) the Van der Waals term becomes significant and deviations from the square root relation arise. This behaviour is observed experimentally as shown in Figure XXVI (page 183) for pyridinium and in Figure XXVII (page 184) for 2-aminopyridinium and anilinium chloride solutions where high surface coverages can be reached and the minimum in $\Delta \bar{G}^0$ consequently be discerned. The results satisfactorily confirm the general basis of the treatment reported previously.³⁰ It may be noted that a similar minimum in the $\Delta \bar{G}^0 - \theta^{3/2}$ curve for the neutral quinoline molecule was also observed experimentally at high surface coverages (cf. Figure XXXI b).

(vi) Surface Charge and Changes of the E.C.M. Potential

Changes, ΔE , of the potential of the e.c.m. are shown in Figure XXVIII, page 185 as a logarithmic function of concentration c of the various organic ions. ΔE is linear in $\log c$ but the slopes of the lines vary with the molecular structure of the ions. It is striking that for the least " π -deficient" ions, 2-aminopyridinium and anilinium, the shifts of the e.c.m. are small or negligible whilst for the hydrogenated derivatives having smaller - or no - π -orbital character the slopes $d \Delta E / d \log c$ are the largest. These data thus indicate in another way that the least " π -deficient"

Figure XXVI: Dependence of the standard electrochemical
free energy of adsorption $\Delta \bar{G}^0$ at various electrode
potentials upon $\theta^{1/2}$ for pyridinium chloride.

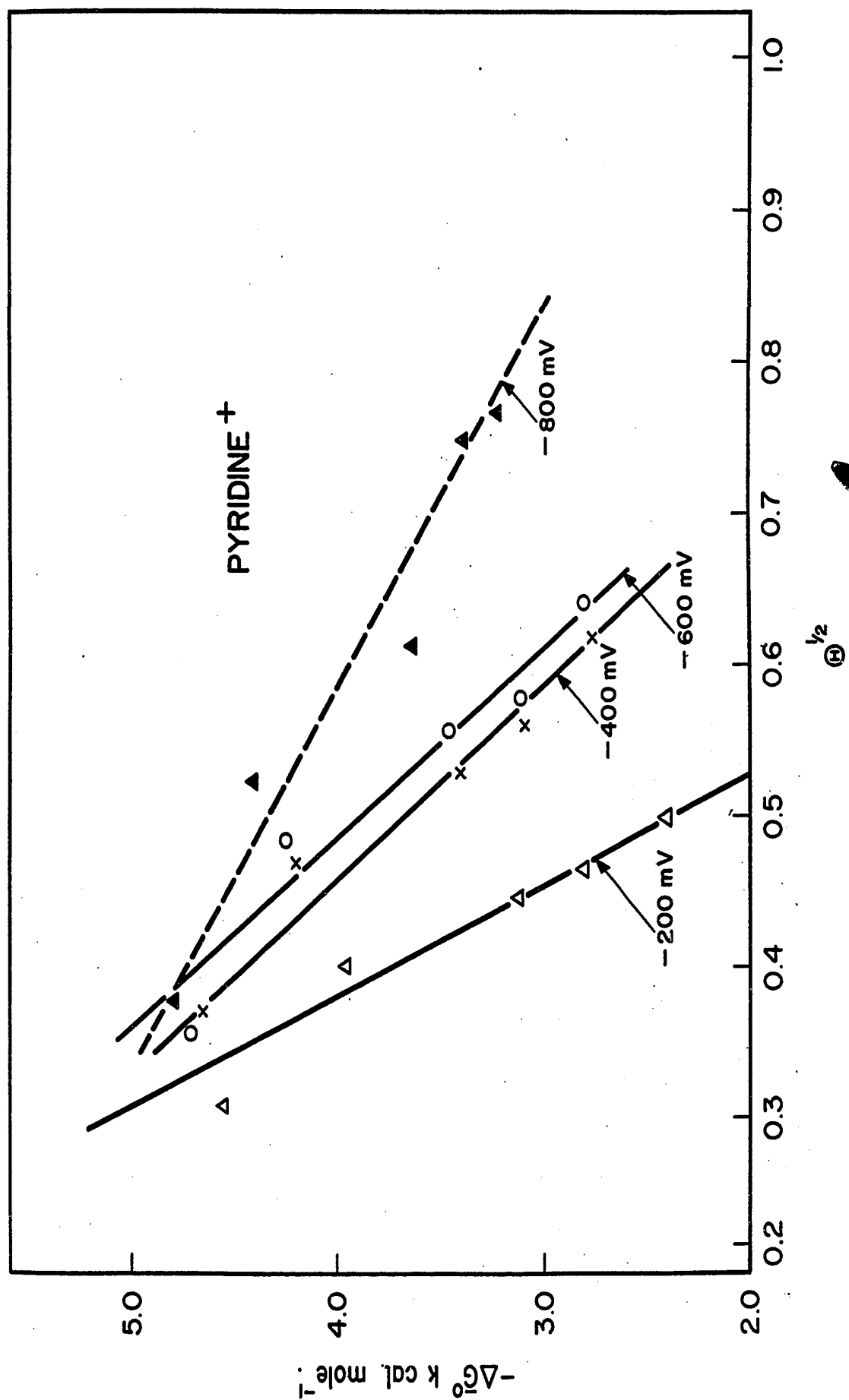


Figure XXVII: Dependence of the standard electrochemical free energy of adsorption $\Delta \bar{G}^0$ at various electrode potentials upon $e^{1/2}$ for 2-aminopyridinium and anilinium chlorides.

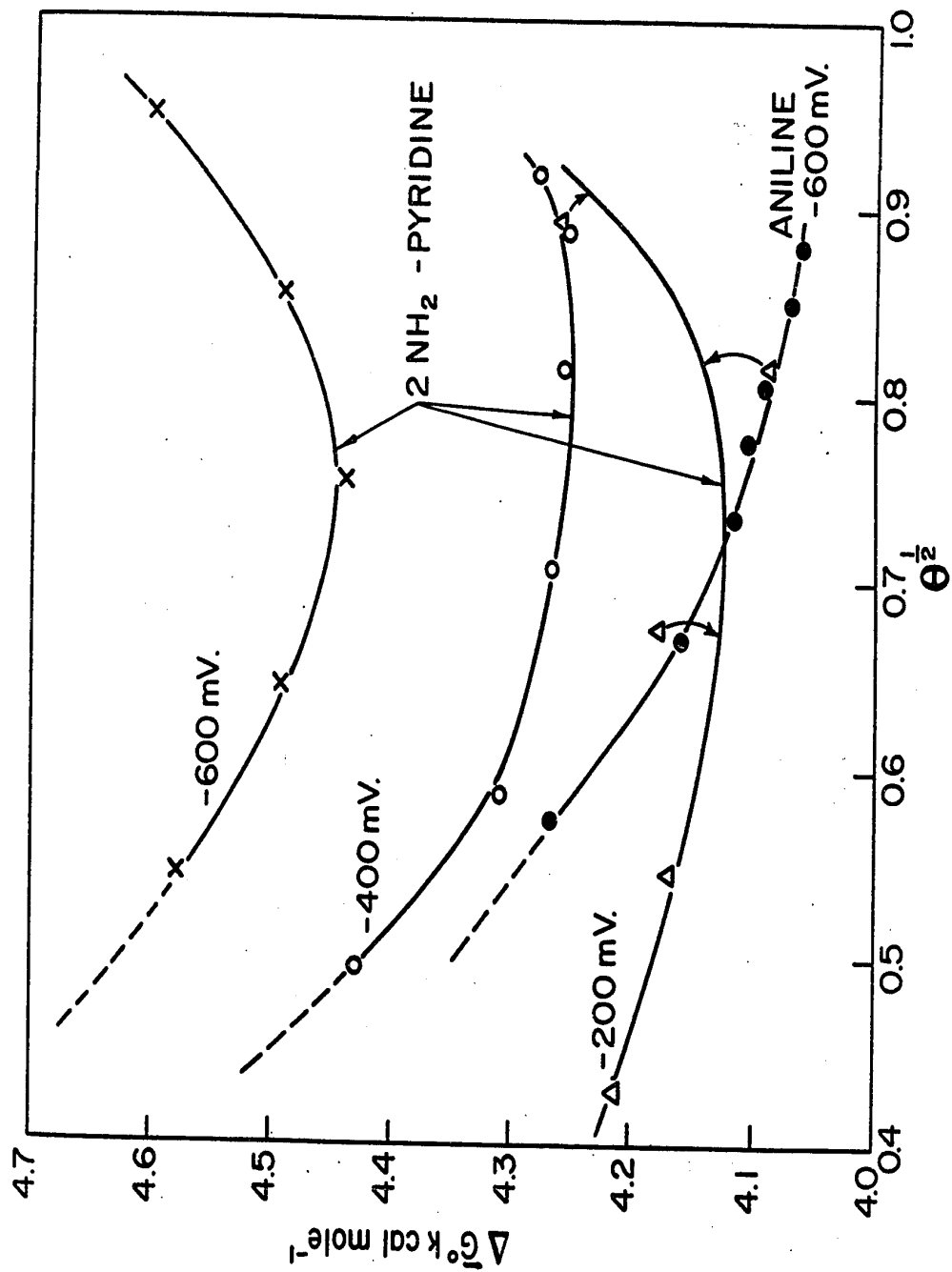
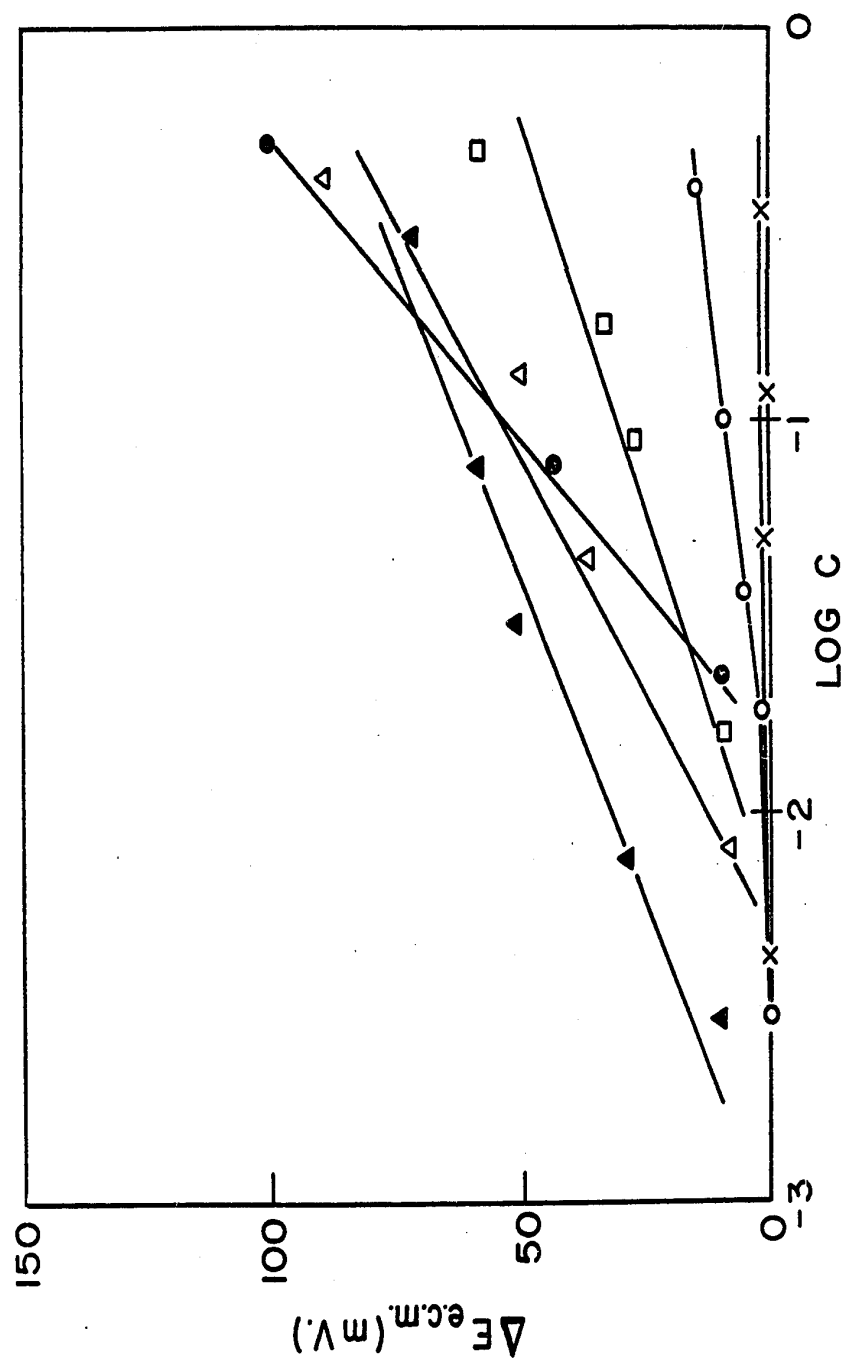


Figure XXVIII: Changes of the potential of the e.c.m. in the presence of the aminium ions in N HCl (Esin and Markov effect) as a function of logarithm of the adsorbate concentration.

O Anilinium;	X 2-aminopyridinium;
● piperidinium;	△ 1,2,3,6-tetrahydropyridinium;
▲ 2-chloropyridinium;	□ pyridinium.



ions are adsorbed "symmetrically" about the e.c.m.; on the negative branch due to ordinary ion-field electrostatic effects and on the positive branch due to π -orbital interaction with the positive Hg surface. Related conclusions were drawn in Section A for the corresponding neutral bases. The values of $\Gamma_{\max}$ from the isotherms for the bases in ionic form correspond most closely to "flat" orientation at the metal, i.e., where maximum π -orbital overlap with the metal surface orbitals can occur. Values* of $d \Delta E_{e.c.m.} / d \log c$ vary from about 0.003 V to 0.065 V; most values are less than 2.3 RT/F, as found e.g. for alkali metal salts with specifically adsorbed anions.²⁷ (vide infra)

The surface charges q_M on the metal for various concentrations of the ions and over a range of electrode potentials, are shown in Figures XXIX page 187. For anilinium and 2-aminopyridinium chlorides the q_M values are hardly changed from those for the primitive HCl solution and the Γ_A values are almost independent of electrode potential. For piperidine ions having no conjugation the effects on q_M are somewhat larger and Γ_A values are more dependent upon electrode potential. The π -deficient pyridinium ion shows an

* A more detailed thermodynamic analysis of these values follows in the section on the "Esin and Markov" effect (p. 212).

Figure XXIX:

Surface charge q_M on the mercury electrode and surface excess Γ_A of adsorbate (i.e., $\Gamma_{RHN_3^+} + \Gamma_{RNH_2}$) as a function of concentration and electrode potential for solutions in 1 N HCl,

a) Pyridinium chloride in N HCl;

- N HCl; X $1.57 \times 10^{-2} M$;
- $9.42 \times 10^{-2} M$; Δ $1.89 \times 10^{-1} M$;
- $4.69 \times 10^{-1} M$.

b) Piperidinium chloride in N HCl;

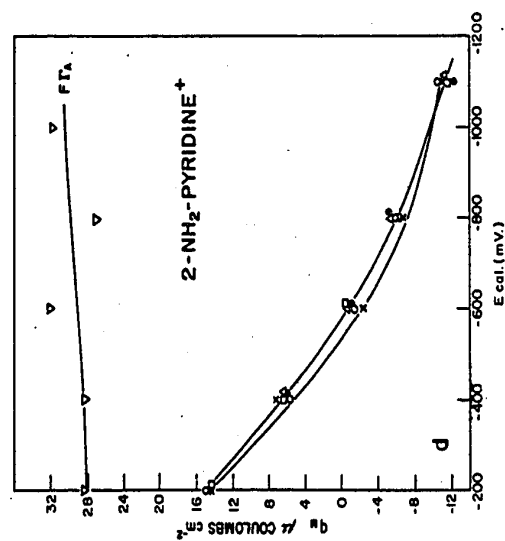
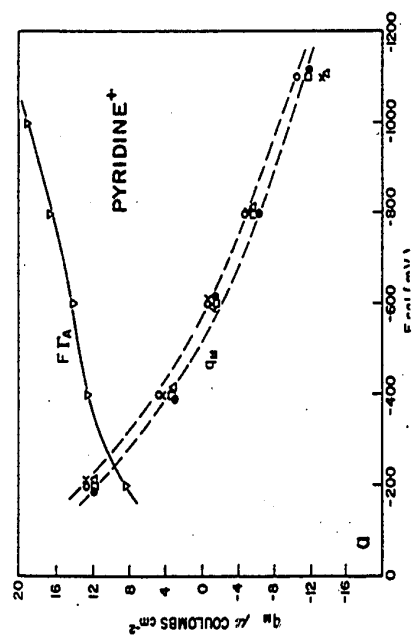
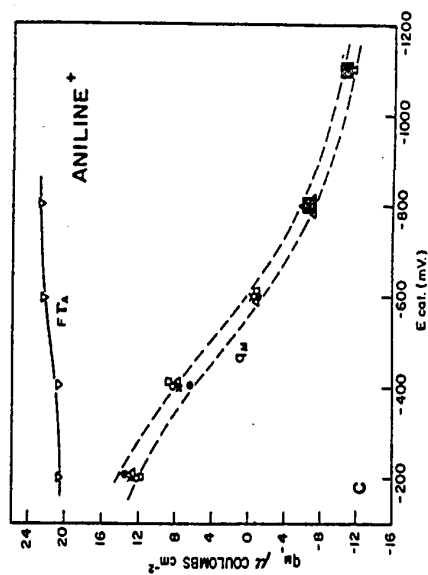
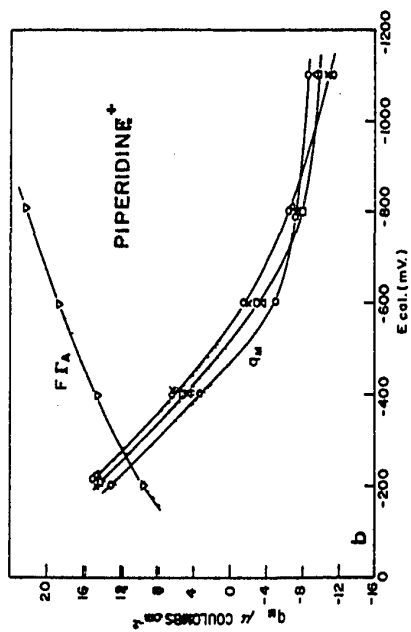
- N HCl; X $2.54 \times 10^{-2} M$;
- $7.94 \times 10^{-2} M$; Δ $1.59 \times 10^{-1} M$;
- $5.50 \times 10^{-1} M$.

c) Anilinium chloride in N HCl;

- N HCl; X $1.20 \times 10^{-2} M$;
- $3.60 \times 10^{-2} M$; Δ $1.01 \times 10^{-1} M$;
- $4.04 \times 10^{-1} M$.

d) 2-Aminopyridinium chloride in N HCl;

- N HCl; X $4.34 \times 10^{-3} M$;
- $5.20 \times 10^{-3} M$; Δ $1.13 \times 10^{-1} M$;
- $3.40 \times 10^{-1} M$.



intermediate degree of variation of Γ_A with potential. The effects with the conjugated ions are again consistent with π -orbital interaction on the positive branch and electrostatic ion-field interaction on the negative branch. Comparison with corresponding charges on the metal in neutral solutions (see Figs. XXIIIa to d (page 161)) shows that the neutral bases have much more effect on q_M (and correspondingly on $-q_s$, the charge on the solution-side of the double-layer) than do the conjugate acid ions. Presumably this arises because in the neutral solutions at high θ the condensed oriented film physically displaces adsorbed ions (see page 212), while in acids, the organic ions can replace the simple inorganic ions normally adsorbed in the double-layer at mercury. These conclusions are supported by determinations of the ionic components of charge in the double-layer to be discussed below.

C. IONIC COMPONENTS OF CHARGE

(1) General remarks

In general, there exists a paucity of data on the ionic components of charge in the electrical double layer. For inorganic adsorbates a few cases have been investigated^{19,30,102} either by electrocapillary or capacity measurements, but with organic adsorbates the situation is much worse. During the progress of the present work it would appear that the only

reported determination of the ionic components of electrical charge for an organic ion system has been that of Bockris and Blomgren³¹ for 2,6-dimethylaniline in 0.1 N hydrochloric acid. The importance of this type of work cannot be underestimated since it leads directly to a detailed knowledge of the structure of the electrical double layer.

In the present work six organic systems have been examined; they are: (1) pyridine in N hydrochloric acid, (2) pyridine in normal potassium chloride, (3) quinoline in N hydrochloric acid, (4) N-methyl pyridinium chloride in 0.33 N hydrochloric acid, (5) N-methyl pyridinium chloride in 1.0 N hydrochloric acid and (6) N-methyl pyridinium chloride in 5.0 N hydrochloric acid.

Typical electrocapillary curves for varying concentrations of pyridine in varying concentrations of hydrochloric acid have been reported in Chapter III. The other sets of electrocapillary curves for the above-mentioned systems have not been shown in order to avoid unnecessary and repetitions presentation of comparatively similar data.

(ii) Pyridine in hydrochloric Acid

A detailed account of the procedure used for evaluating the components of electrical charge has been given in Chapter II (pages 123 - 126). It was shown that the evaluation of equation (105) depends on a knowledge of the variation of $(A \delta)_E$

with respect to $\Delta \log a_{\text{HCl}}$ at constant a_A (or the ratio $a_{\text{py}}/a_{\text{HCl}}$). Figure XXX (a to d) page 191 shows plots of $(\Delta \delta)_{\text{E}}$ against $a_{\text{py}}/a_{\text{HCl}}$ from which actual values of $(\Delta \delta)_{\text{E}, a_{\text{py}}/a_{\text{HCl}}}$ were interpolated. The interpolated values of $(\Delta \delta)_{\text{E}, a_{\text{py}}/a_{\text{HCl}}}$ were then plotted against $\log a_{\text{HCl}}$ (see Figure XXXI) page 192) and from the slopes of these curves, values of Γ_+ were calculated. The values of q_s are obtained [equation (103)] directly from the electrocapillary curves. Having obtained q_s and q_+ (or $F \Gamma_+$), it is a simple matter to calculate q_- (or $-F \Gamma_{\text{Cl}^-}$). Furthermore, $F \Gamma_A$ may be calculated from equation (101) and $F (\Gamma_{\text{H}_3\text{O}^+} - \Gamma_{\text{py}^0})$ may be obtained using equation (79). These five quantities q_s , q_+ , q_- , $F \Gamma_A$ and $F (\Gamma_{\text{H}_3\text{O}^+} - \Gamma_{\text{py}^0})$ for the case of pyridine (at a concentration of 10^{-1}M) in N hydrochloric acid are shown in Figure XXXII page 193 as a function of electrode potential (E_{cal}). q_+ for pyridine in hydrochloric acid is composed of two quantities namely, $F (\Gamma_{\text{H}_3\text{O}^+} + \Gamma_{\text{py}^+})$, and as previously mentioned in Chapter II, there is no (thermodynamic) means of determining either of the two quantities individually. The value of q_+ increases slowly from + 0.2 microcoulombs at - 200 mV to a steady value of about + 4.0 microcoulombs for the potential range of - 600 to - 1200 mV. This can be interpreted either as a result of a predominant

Figure XXX: Plots of $(\Delta\epsilon)_{\text{cal}}$ vs $a/a_{\text{py HCl}}$ for

- a) Pyridine in 0.1 N HCl
- b) Pyridine in 0.33 N HCl
- c) Pyridine in 1.0 N HCl
- d) Pyridine in 5.0 N HCl.

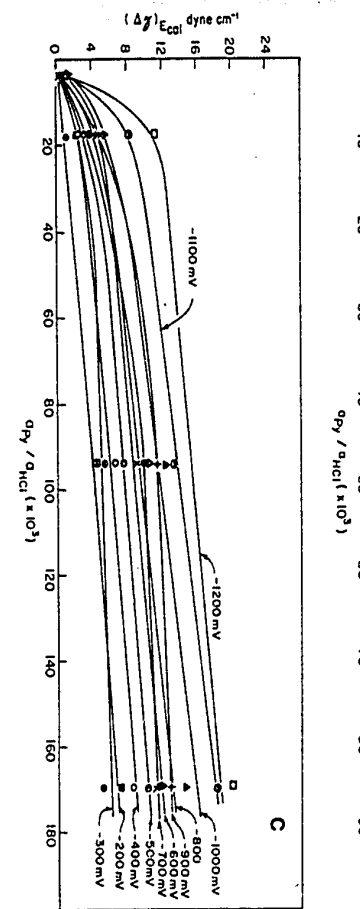
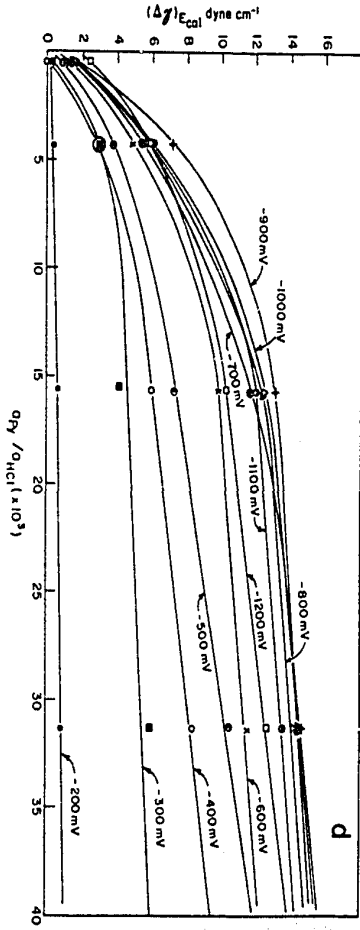
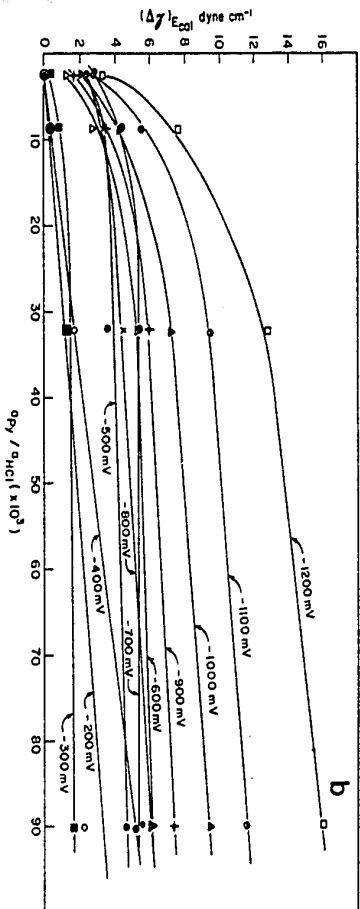
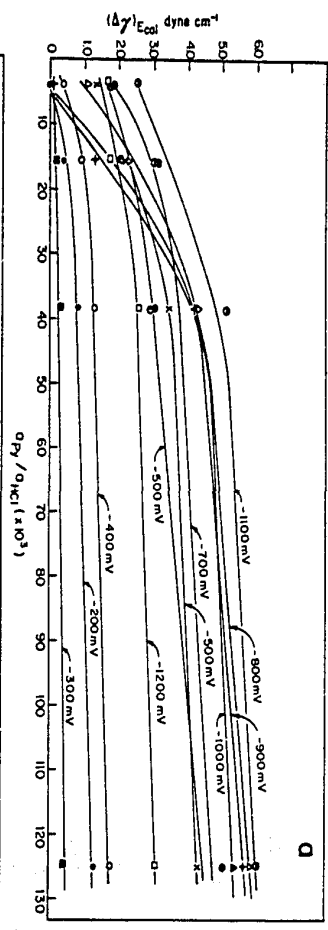


Figure XXXI: Plots of $(\Delta\gamma)_{a_{\text{Py}}/a_{\text{HCl}}}$ E_{cal} vs
 $\log a_{\text{HCl}}$ for pyridinium chloride.

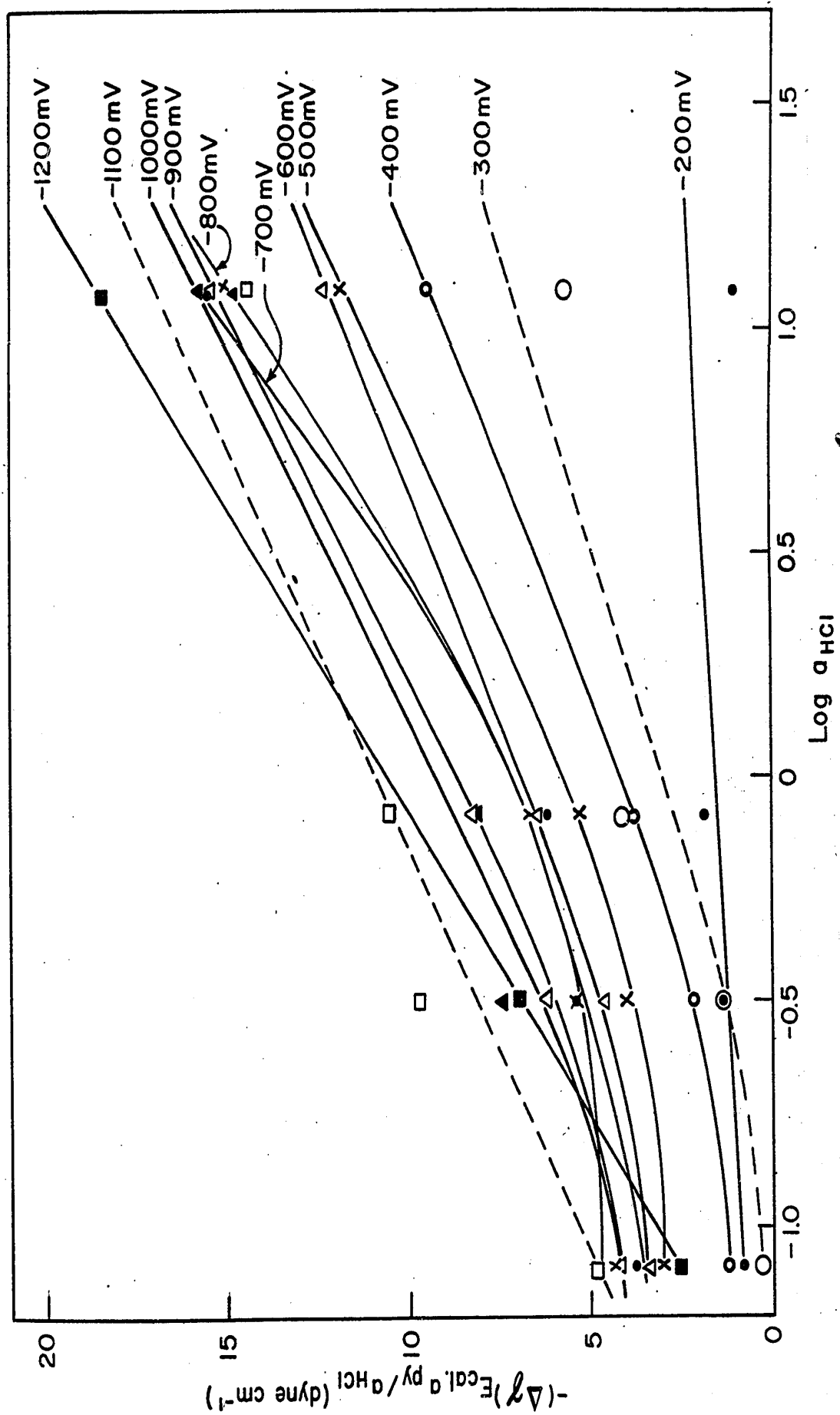
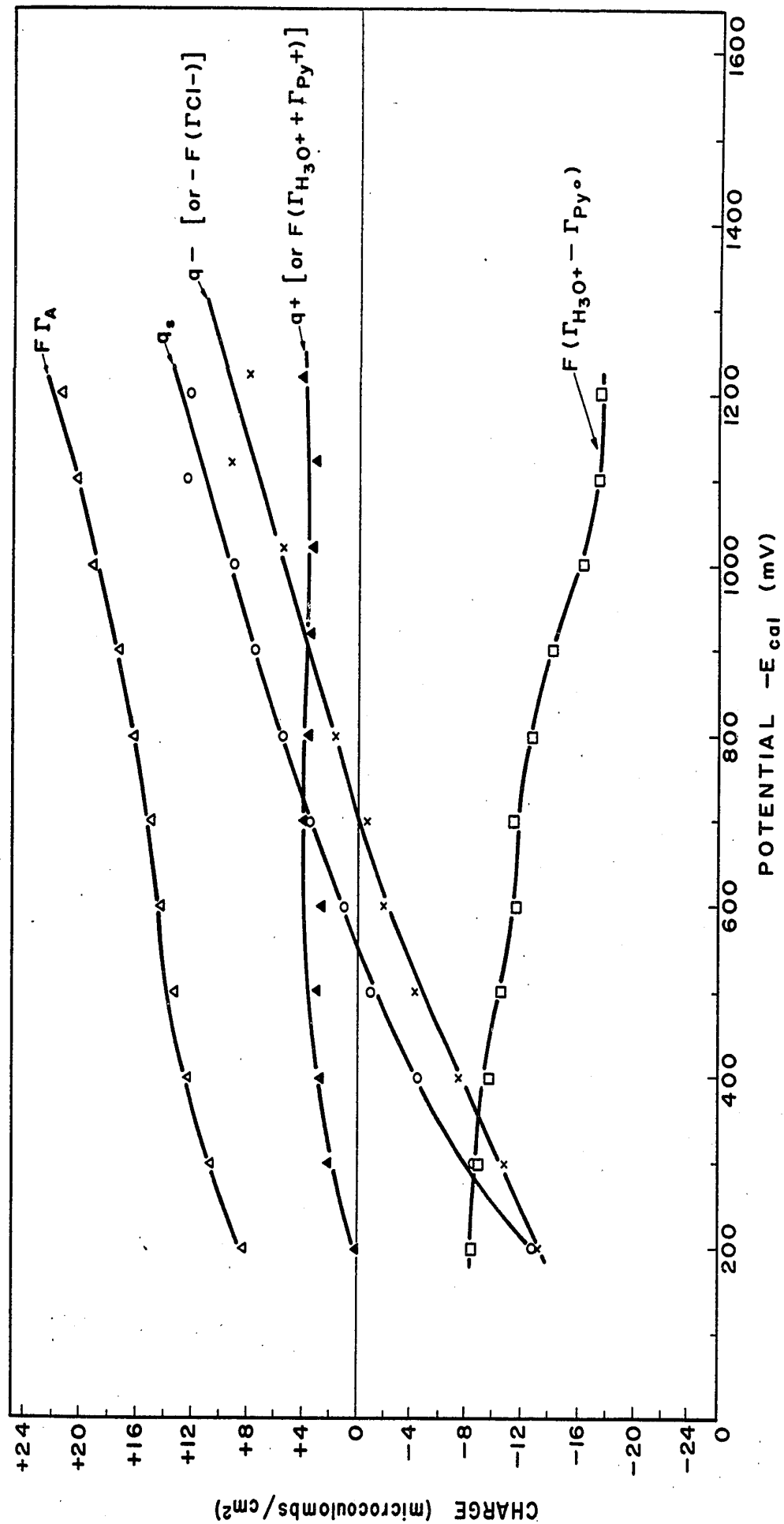


Figure XXXII: Ionic components of charge for pyridine
in hydrochloric acid as a functions of electrode
potential ($C_{py} = 10^{-1}M$, $C_{HCl} = 1 N$).



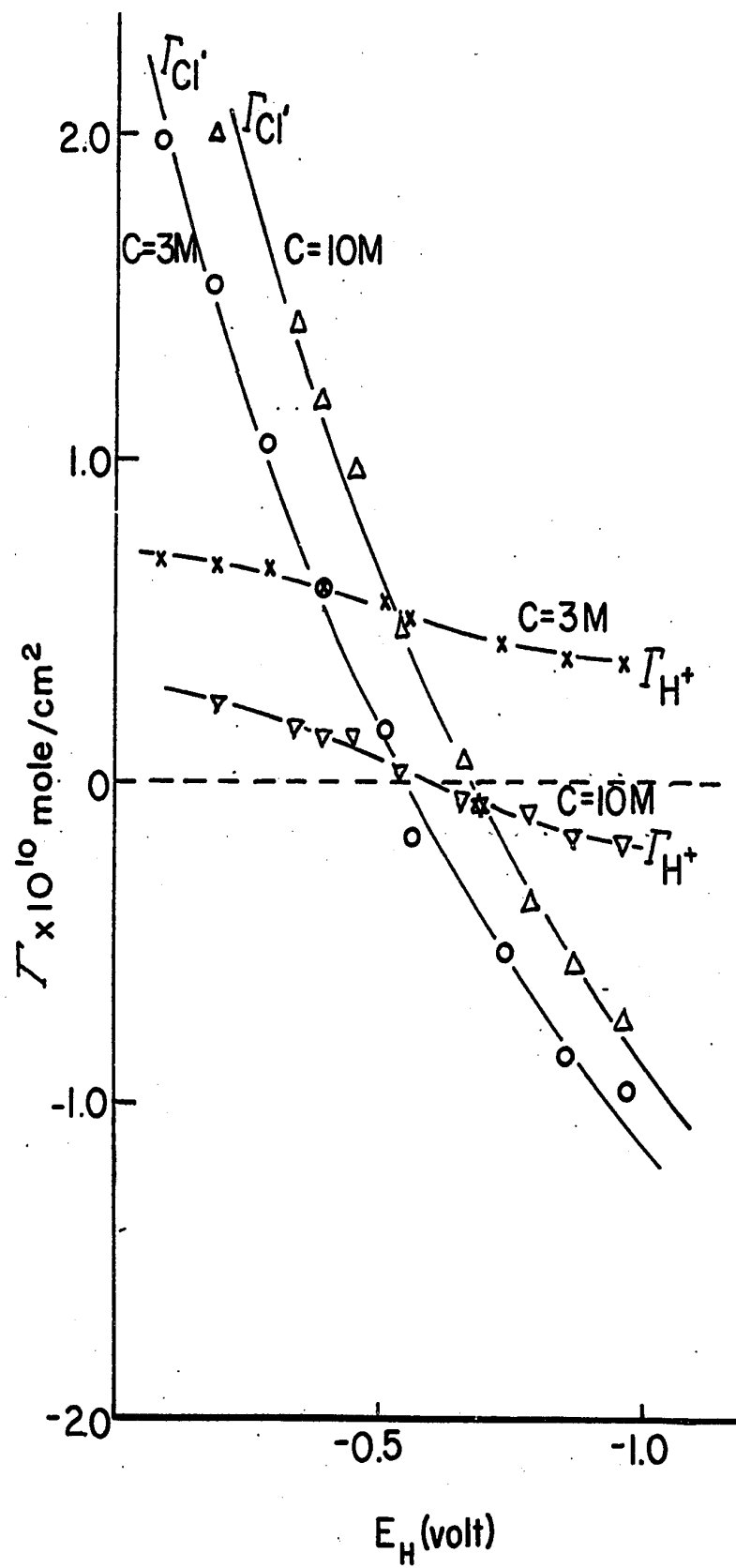
adsorption of pyridinium ions (py^+) or as a result of an increase of the surface excess of H_3O^+ ions over that present when the interface is in contact with aqueous N hydrochloric acid. It is suggested here that the enhanced values of q_+ are due essentially to an increase in Γ_{py^+} and not $\Gamma_{\text{H}_3\text{O}^+}$. The quantity $F \Gamma_{\text{py}^+}$ is probably a specifically adsorbed charge, and supporting evidence for this conclusion, based on components of charge in N-methyl pyridinium chloride solutions, will be given below (see C (iv), this chapter).

The values of q_- at anodic potentials relative to the e.c.m. indicate that Γ_{Cl^-} is positive, but at increasingly negative potentials (i.e. beyond -700 mV), it will be seen that Γ_{Cl^-} becomes negative. The latter behaviour may appear to be normal (since Cl^- ions will be repelled out from the double layer on the negative branch) were it not for the fact that $F (\Gamma_{\text{H}_3\text{O}^+} - \Gamma_{\text{py}^0})$ is a negative quantity over the entire potential range. Since it has been suggested that much of the value of $F \Gamma_A$ must be due to $F \Gamma_{\text{py}^+}$ then it would seem that $F \Gamma_{\text{py}^0}$ should be a small or negligible quantity. If this is so, then $F \Gamma_{\text{H}_3\text{O}^+}$ would indeed be negative (as it is in the unambiguous case of N-methyl pyridinium solutions). Under these conditions we would apparently observe an anomalous situation where both Γ_{Cl^-}

and $\Gamma_{H_3O^+}$ are negative, indicating a surface deficiency of both H_3O^+ and Cl^- ions in the double layer. This result appears to be unreasonable and inexplicable on any simple view of the double layer.

However, Frumkin and Jofa¹⁰² have also reported the same anomaly in their observations of the ionic components of charge for a simpler system - strong hydrochloric acid solutions (3 N and 10 N) at mercury. Figure XXXIII page 196 demonstrates the results obtained by these authors. It is to be noted that for 10 N HCl, Γ_{Cl^-} and $\Gamma_{H_3O^+}$ are both negative at potentials cathodic to the e.c.m. The following qualitative explanation may be offered for this apparent anomaly which was not further discussed in the original paper. Γ_{Cl^-} and $\Gamma_{H_3O^+}$ would be negative if the activity of water increased near the metal surface in the high field of the double layer. This is in fact possible since U_{H_2O} (the energy of water in the electrode field) can be of the order of 1 to 3 kcal mole⁻¹. hence H_2O molecules may be "electrochemically" adsorbed and their activity increased in the double layer. In the case of the high acid concentrations investigated by Frumkin and Jofa there is virtually no diffuse double layer so that the potential of the outer Helmholtz layer ϕ_2 (q.v. Chapter I) is zero with respect to that in the bulk of the solution and the apparent deficiency of both H_3O^+ and Cl^- ions

Figure XXXIII: Components of charge for hydrochloric acid as functions of electrode potential ($C = 3\text{ N HCl}$ and 10 N HCl). Data reproduced from A.N. Frumkin and S. Jofa, *Acta Physicochimica, U.R.S.S.*, 10, 353 (1939).



could only be explained in this simple case by such a mechanism of the increase in the activity of water in the double layer at high fields.

On the basis of the results for pyridine solutions in hydrochloric acid shown in Figure XXXII alone it may be equally plausible to suggest that the large negative values of $F (\Gamma_{H_3O^+} - \Gamma_{py^0})$ may be due entirely to positive values Γ_{py^0} and that the neutral molecule is the adsorbed species reflected in $F \Gamma_A$. If this is true, then the foregoing anomaly would disappear since $\Gamma_{H_3O^+}$ would then be zero or probably slightly positive. However, we also have evidence from the present work to be presented later (q.v. section C (iv) this Chapter) which indicates quite clearly that $\Gamma_{H_3O^+}$ may reasonably be assumed to be large and negative. Before proceeding to elaborate on this evidence we first examine the behaviour of quinoline solutions in hydrochloric acid.

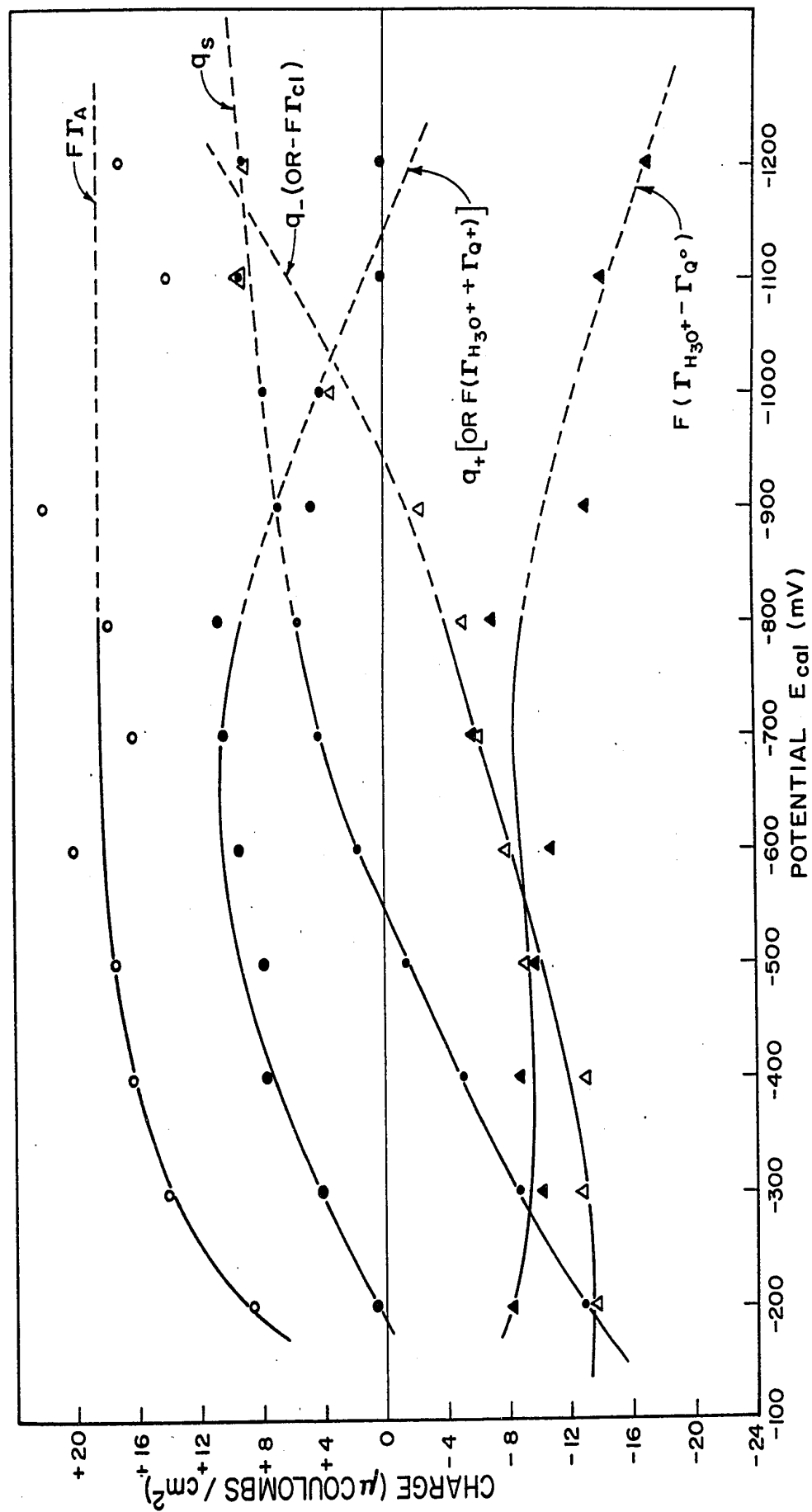
(iii) Quinoline in Hydrochloric Acid

The ionic components of charge for quinoline have been derived from a similar set of electrocapillary curves and calculations as that shown above for pyridine, and they are shown in Figure XXXIV page 198. It must be stated

Figure XXIV:

Components of charge for quinoline in hydrochloric acid as functions of electrode potential.

($C_{Q^+} = 3.9 \times 10^{-3} M$ and $C_{HCl} = 1.0 N$).



at the outset that the values beyond a potential of - 800 mV. (shown on Figure XXXIV as dotted lines) are not very significant. This is due to the uncertainty in values of the surface tension at high negative polarisations. At low concentrations of quinoline and hydrochloric acid the experimental determinations of the electrocapillary curves are quite easy to make up to potentials of about - 1000 mV; at higher concentrations of quinoline and hydrochloric acid experimental difficulties were encountered due to discharge of the quinolinium ions, this effect being first noticeable at polarisations on the negative branch beyond - 800 mV. The discharge of the adsorbate ions tends to block the capillary probably because of the relative insolubility of the neutral molecules as compared with that of the ions. Furthermore, at concentrations of hydrochloric acid of about 5 N, there is a greater tendency for hydrogen gas to be liberated (q.v. "electrocapillary viscosity" effect, Chapter I). The two effects reinforce each other at high cathodic potentials, and the net result contributes to the uncertainty of the experimental determinations under these conditions.

Again, as in the case of pyridine, the values of q_+ are positive and increasing from low potentials to about - 750 mV, but beyond this point q_+ drops steadily to a negative value at about - 1150 mV. The most significant result is that $F (\int_{H_3O^+} - \int_{Q^0})$ is negative throughout the whole potential

range investigated. It is once more suggested that Q^+ ions are specifically adsorbed at the mercury surface even at positive potentials relative to the e.c.m. This will mean that Γ_{Q^0} is either zero or a very small positive quantity. This conclusion is again based on the evidence to be presented below that $\Gamma_{H_3O^+}$ in these systems is a large and negative quantity as mentioned in the above discussion on the components of electrical charge for pyridine in hydrochloric acid.

(iv) N-Methyl pyridinium Chloride in Hydrochloric Acid

This system was chosen in order to provide further information which might elucidate the anomalous behaviour observed in the pyridinium and quinolinium solutions and which leads to a direct and unambiguous evaluation of $\Gamma_{H_3O^+}$. The calculations for the components of electrical charge for N-methyl pyridinium chloride in hydrochloric acid solutions are easier than those for quinoline and pyridine. The requirement of maintaining the activity of the adsorbate (a_A) constant presents less difficulty in this case since there is no acid-base proton equilibrium to be considered. Thus, it is not necessary to interpolate surface tension values at constant ratios of a_{BH^+}/a_{HCl} as in the cases of pyridine and quinoline. The concentration of N-methyl

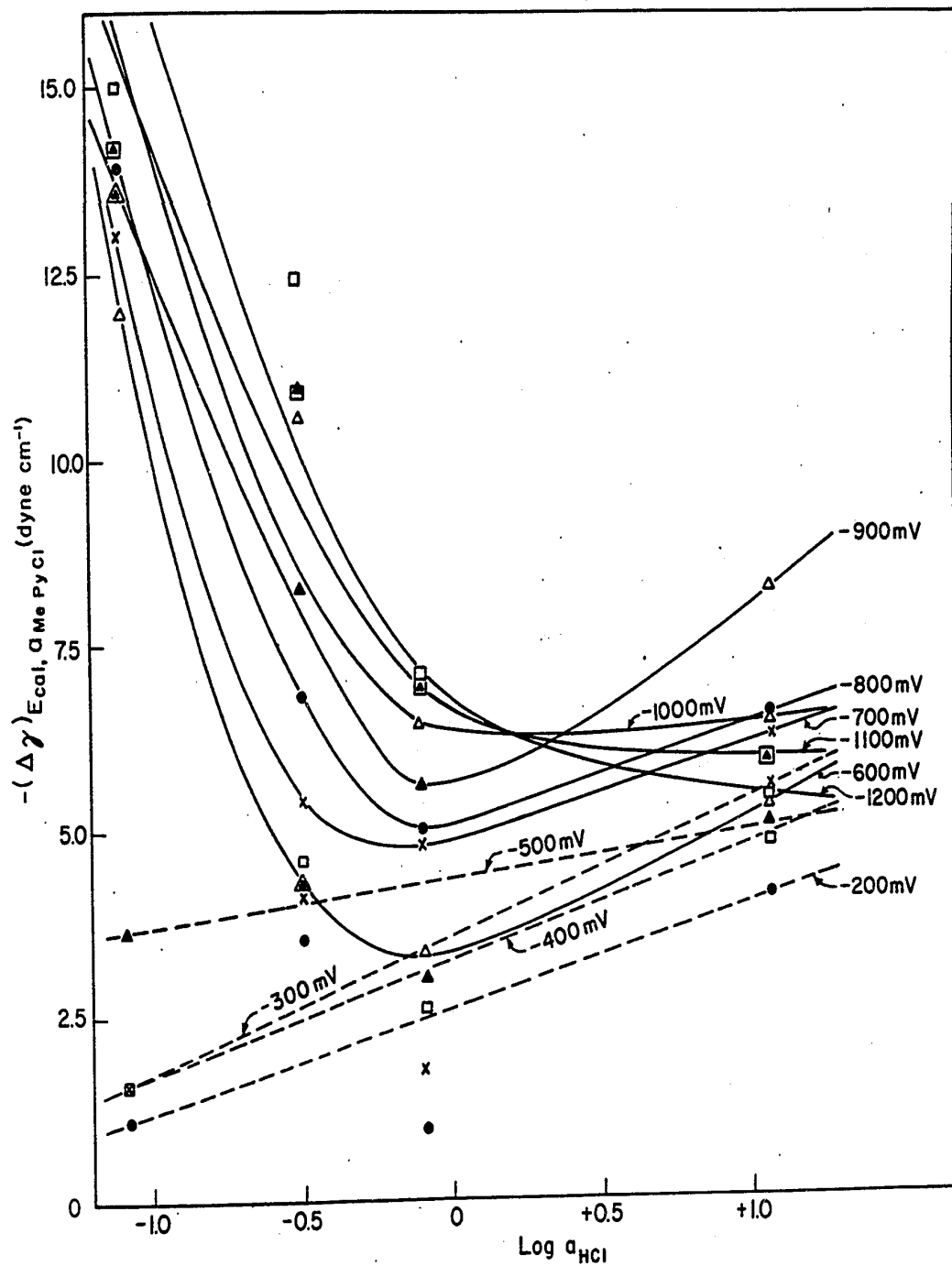
pyridinium ions (MePy^+) is not dependent on the variation in activity of hydrochloric acid. Hence, the slope of the curves obtained by plotting $(\Delta\gamma)_{E_{\text{cal}}, a_{\text{MePyCl}}}$ against $\log a_{\text{HCl}}$ (see Figure XXXV, page 202) will provide direct information for the calculation of q_+ values. Since a_{MePyCl} is kept constant, $(\Delta\gamma)_{E_{\text{cal}}, a_{\text{MePyCl}}} / 2.3RT \log a_{\text{HCl}}$ will give a direct and unambiguous determination of $\gamma_{\text{H}_3\text{O}^+}$. The values of q_+ are therefore equal to the respective sums of $F \gamma_{\text{H}_3\text{O}^+} + F \gamma_{\text{MePy}^+}$ values, and the latter quantities are directly obtainable from an estimate of $F \gamma_{\text{A}}$ (or $F \gamma_{\text{MePyCl}}$) at constant activity of HCl.

Inspection of Figure XXXV shows that at potentials greater than -500 mV, the slopes of the curves change sign for increasing and decreasing values of a_{HCl} around about $\log a_{\text{HCl}} = -0.1$. This is a real but somewhat unexpected result; careful estimates of the maximum experimental error in the determination of the electrocapillary curves indicate that $(\Delta\gamma)_{E_{\text{cal}}, a_{\text{MePyCl}}}$ values are accurate to within $\pm 0.7 \text{ dynes cm}^{-1}$; such an error may affect the exact values of $\gamma_{\text{H}_3\text{O}^+}$ deduced but cannot change the sign of the slopes of the curves in Figure XXXV.

The ionic components of charge for N-methyl pyridinium chloride ($a_{\text{MePyCl}} = 10^{-2} \text{M}$) in 0.33 N, 1.0 N and 5.0 N hydro-

Figure XXXV:

Plots of $(\Delta\epsilon)_{\text{cal}}^{\text{MePyCl}}$ vs $\log a_{\text{HCl}}$ for
N-methyl pyridinium chloride at various hydrochloric
acid concentrations.



chloric acid solutions are shown in Figures XXXVI, XXXVII and XXXVIII respectively (pages 204-206). The most important results of these findings are the actual values of $\int \text{H}_3\text{O}^+$ at various acid concentrations.

The case of N-methyl pyridinium chloride in 5.0 N hydrochloric acid presents the most reasonable experimental results in terms of a simple double layer picture. q or $-F \int \text{Cl}^-$ is shown in Figure XXXVIII to be negative, which implies that there exists a surface excess of chloride ions in the double layer (i.e. $\int \text{Cl}^-$ is positive). This result is consistent with the slightly positive (0 to + 3.0 μ -coulombs cm^{-2}) values of $F \int \text{H}_3\text{O}^+$ (presumably a diffuse layer charge) over a wide range of electrode potentials. However, it may be pointed out that at highly negative potentials (> -1150 mV) $\int \text{H}_3\text{O}^+$ tends to become slightly negative and this is understandable if at high cathodic potentials ϕ_2^* becomes positive due to specific adsorption of the organic cation. The order of magnitude of values of $\int \text{H}_3\text{O}^+$ appears to be similar to that of the corresponding data given by Frumkin and Jofa for 3 N and 10 N hydrochloric acids (in the absence of any organic additives). Since $F \int \text{H}_3\text{O}^+$ is not greater than about 3 μ -coulombs cm^{-2} , we may conclude that the main contribution to q arises from the specifically

* If the specifically adsorbed cation were to suffer significant dehydration (but see p. 172) the potential referred to here should be ϕ_1 rather than ϕ_2 (Fig. 2).

Figure XXXVI:

Ionic components of charge for N-methyl pyridinium
chloride in 0.33 N hydrochloric acid solution as
functions of electrode potential ($C_{\text{MePyCl}} = 2 \times 10^{-2} \text{M}$).

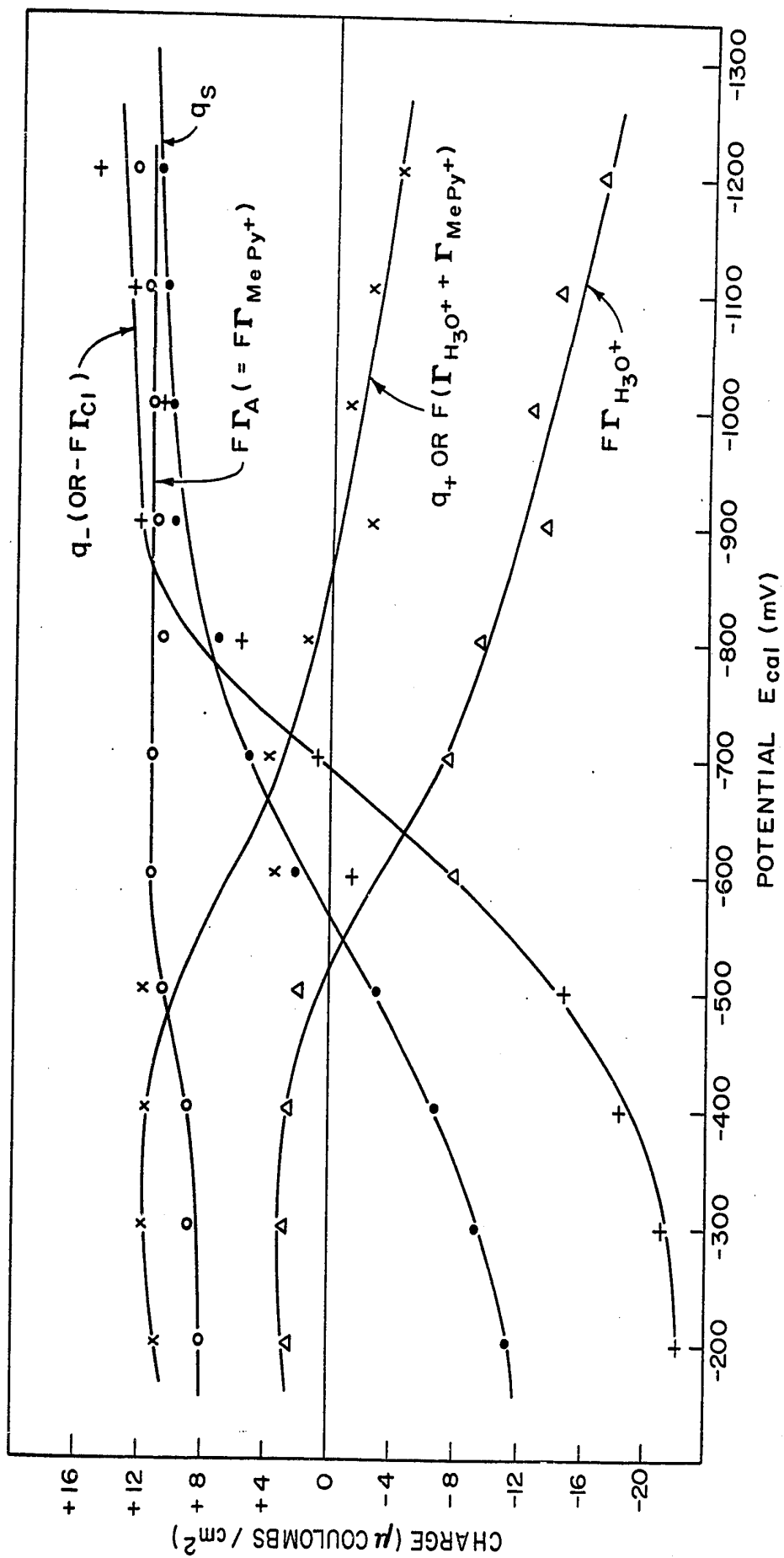


Figure XXXVII:

Ionic components of charge for N-methyl pyridinium
chloride in 1.0 N hydrochloric acid solution as
functions of electrode potential. ($C_{\text{MePyCl}} = 2 \times 10^{-2} \text{ M}$).

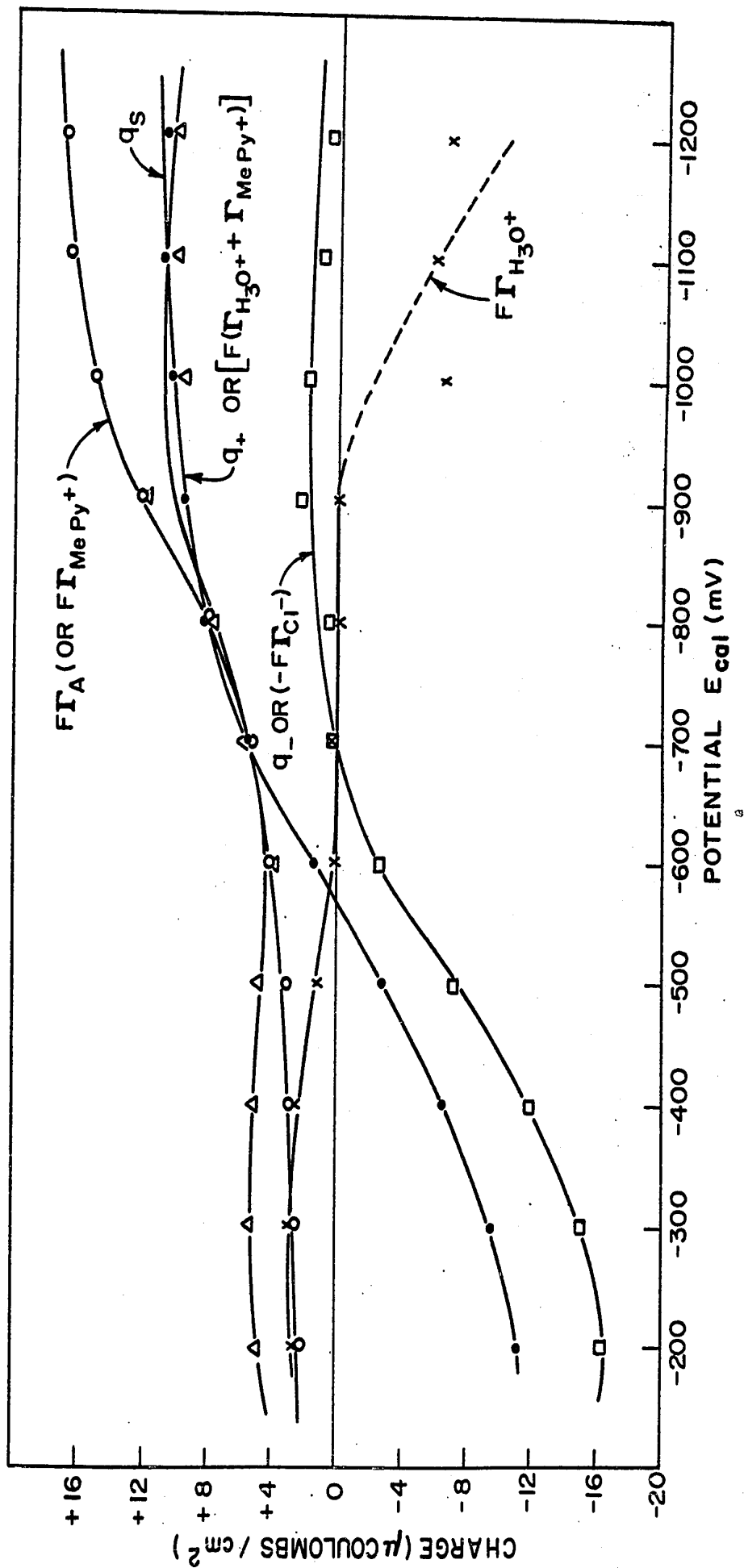
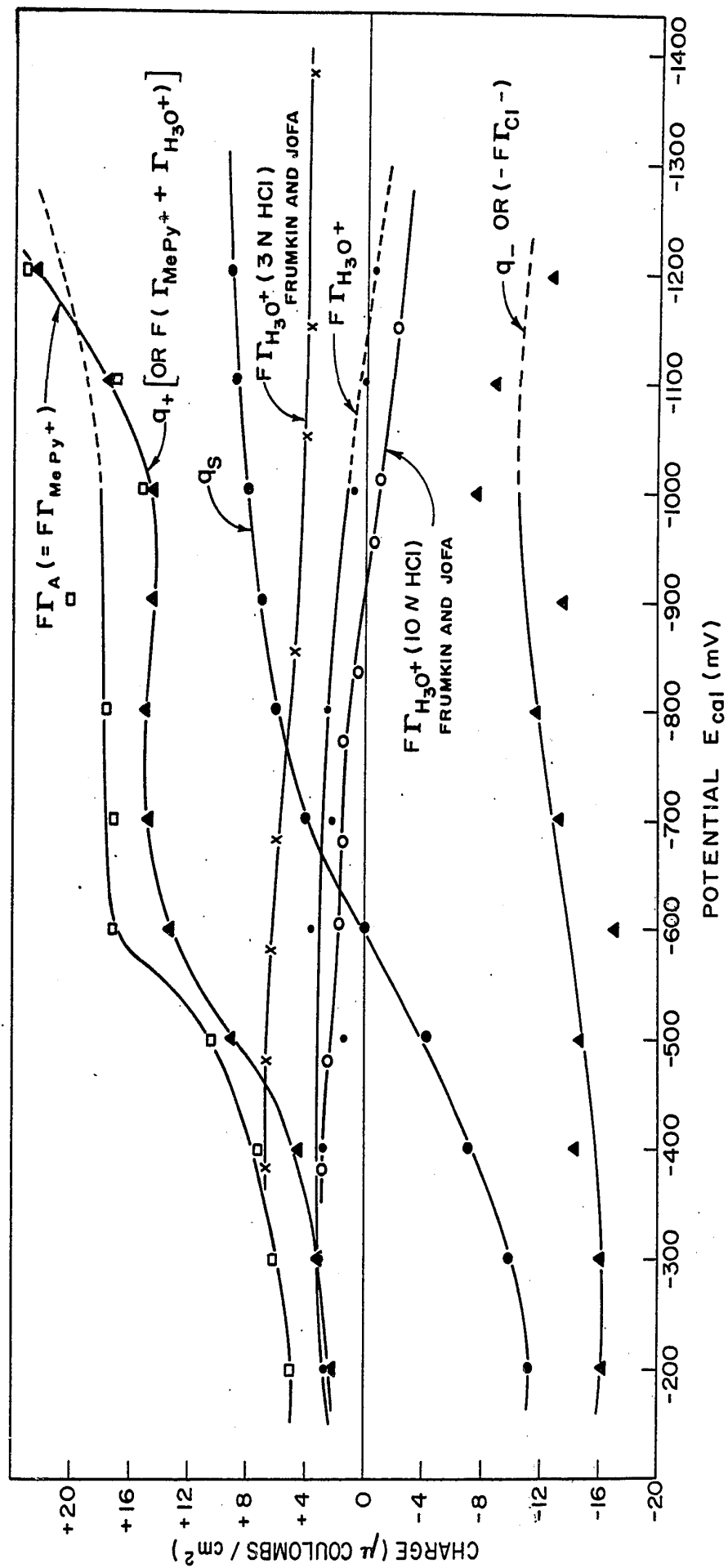


Figure XXXVIII:

Ionic components of charge for N-methyl pyridinium
chloride in 5.0 N hydrochloric acid solutions as
functions of electrode potentials ($C_{\text{MePyCl}} = 2 \times 10^{-2} \text{ M}$).



adsorbed MePy⁺ ions. This is obvious from inspection of the high and increasing positive values of q_+ or $F(\Gamma_{H_3O^+}^{MePy^+} + \Gamma_{H_3O^+})$; since $\Gamma_{H_3O^+}$ is small, it is clear that $\Gamma_{H_3O^+}^{MePy^+}$ is large and positive over most of the potential range investigated. The deficiency of H_3O^+ in the diffuse double layer at high negative polarisations necessitates that ϕ_2 , the potential at the outer Helmholtz layer, be positive (E - ve); hence Γ_{Cl^-} is positive. ϕ_2 is positive in this case due to excess specifically adsorbed cationic charges (MePy⁺). The results are thus rationally interpretable in terms of conventional models of the double layer.

In weaker acid solutions the components of ionic charge for N-methyl pyridinium chloride change with dilution of the acid in a consistent manner. For example, in Figures XXXVI and XXXVII for 1.0 N and 0.33 N hydrochloric acid solutions, there is a tendency for specifically adsorbed anions to be in greater deficiency at the lower concentrations of the acid and this is particularly noticeable at negative polarisation beyond the electrocapillary maximum potential. For 1.0 N hydrochloric acid q_- is slightly positive within -700 mV to -1200 mV (i.e. Γ_{Cl^-} is negative), and for 0.33 N hydrochloric acid Γ_{Cl^-} is more negative indicating therefore a greater surface deficiency with diminution of the acid concentration. Conversely, $\Gamma_{H_3O^+}$ is also more negative

in 0.33 N hydrochloric acid than in either of 1.0 N or 5.0 N hydrochloric acid solutions. As in the case of pyridine and quinoline in hydrochloric acid, we observe once more the anomaly of both $\Gamma_{H_3O^+}$ and Γ_{Cl^-} being negative at high cathodic polarisations, but in this case $\Gamma_{H_3O^+}$ is known directly and not as part of the term $F(\Gamma_{H_3O^+} - \Gamma_{Py^0})$.

This is a puzzling result and no simple explanation can adequately account for this unexpected behaviour. From a qualitative standpoint, it may be speculated that the suggested mechanism of increased activity of water in the double layer at high fields (as discussed above for Frumkin and Jofa's results) could also be applicable here.

The most important conclusion to be drawn from the results for N-methyl pyridinium chloride in hydrochloric acid solutions is the fact that $\Gamma_{H_3O^+}$ is, for most of the potential range examined, negative (or positive only to a very small extent-less than $3.0 \mu\text{-coulombs cm}^{-2}$). This provides strong corroborative evidence for supporting the contention that in acid solutions of the heterocyclic bases the species predominantly adsorbed at the mercury interface is mainly the organic cation and not the neutral molecule. This is also the conclusion of Blomgren and Bockris (loc cit) with regard to adsorption of dimethylaniline from hydrochloric acid solutions. It may

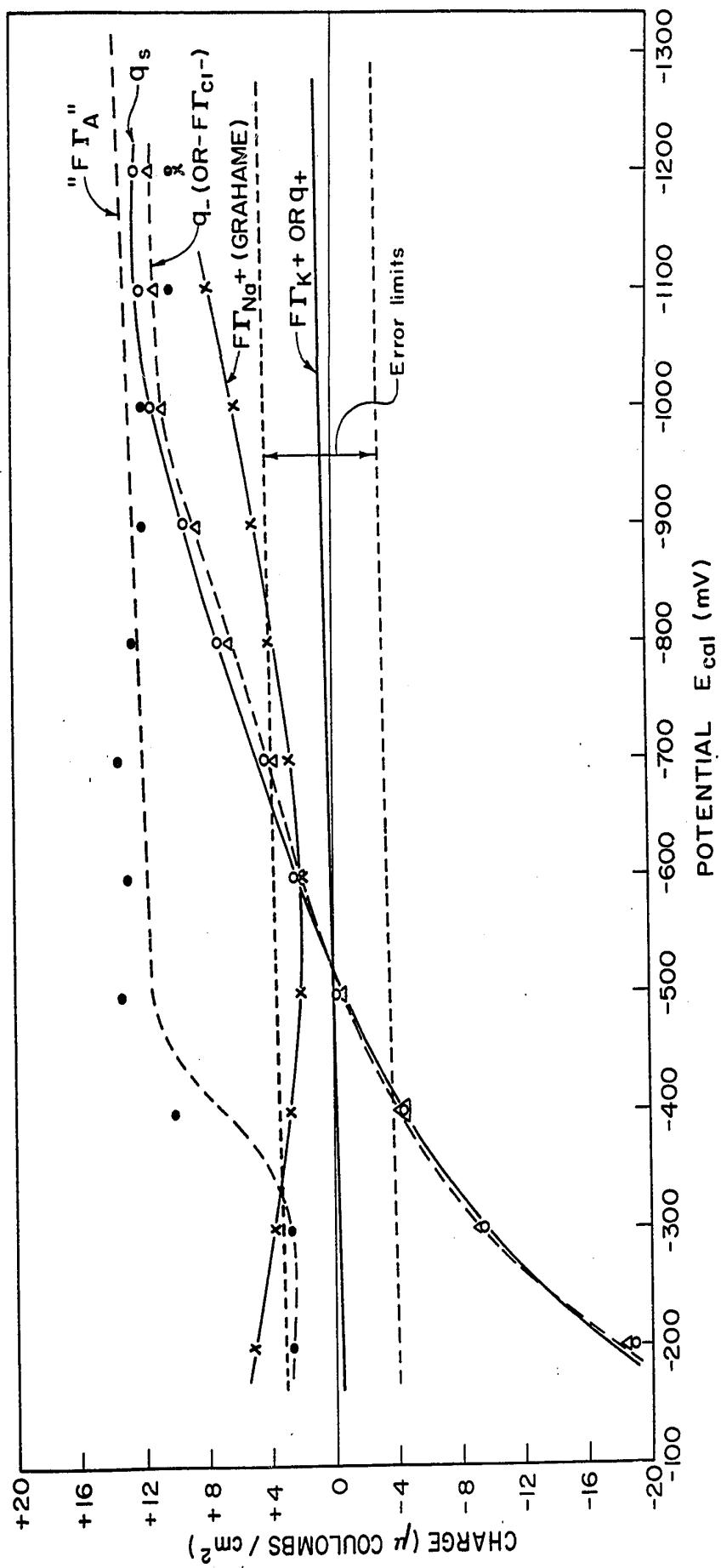
also be noted that since we have shown that the isotherms for the adsorption of the organic bases in acid solution can be represented by equation (133) with $\Delta \bar{G}^0$ decreasing linearly with $\theta^{1/2}$ (e.g. see Figure XXVI), it follows that adsorption of the additive as the ion rather than the neutral molecule is occurring in these cases, since equation (133) is deduced for ionic repulsions. It cannot be assumed, however, that the above is a general result for acid solutions of amines since the heterocyclic ions studied in the present work have a π -orbital at the N^+ atom which will not be available in the same way in aliphatic amine ions.

(v) Pyridine in Potassium Chloride Solutions

The components of charge for pyridine ($10^{-2}M$) in a 0.3 M potassium chloride solution are shown in Figure XXXIX page 210. The values of q_- or $-F(\int_{Cl^-})$, are negative at potentials anodic to the e.c.m. and positive at potentials cathodic to the e.c.m. This is quite consistent with the fact that at positive potentials the Cl^- ions are specifically adsorbed and at negative potentials the ions are repelled from the double layer. The values of $"F \int_A"$ remain positive throughout the range of potentials examined, and have been plotted as a matter of comparative interest (and to include them on the same scale as that for the q values) on the

Figure XXXIX:

Ionic components of charge for pyridine in 0.3 N KCl
as functions of electrode potential ($C_{Py^0} = 3 \times 10^{-2} M$).



assumption that such will be the values of $F \sqrt{A}$ if the neutral molecule possessed an imaginary unit positive or negative charge. The actual experimental points for the values of q_+ or $F \sqrt{K^+}$ fluctuate within a rather wide range of uncertainty and as a result of this the curve shown in Figure XXXIX represents the statistically calculated probable line for q_+ . The equation for this straight line ($y = mx + c$) was obtained from the following equations:

$$m = \frac{n \sum (xy) - \sum y \sum x}{n \sum (x^2) - (\sum x)^2} \quad (134)$$

$$c = \frac{\sum x^2 \sum y - \sum x \sum (xy)}{n \sum (x^2) - (\sum x)^2} \quad (135)$$

where m is the slope of the line and c the intercept. n is the number of experimental points, x and y are the abscissa and ordinate values, respectively. The theoretical line $y = mx + c$ was drawn and values for δ (the standard deviation) of all points deviating from the line were measured whereupon the probable error in m , i.e. α_m and the probable error in c i.e., α_c were calculated according to the following equations:

$$\alpha_m = 0.67 \left\{ \frac{n \sum (\delta)^2}{(n - 2) [n \sum x^2 - (\sum x)^2]} \right\}^{1/2} \quad (136)$$

$$\alpha_c = 0.67 \left\{ \frac{\sum (\delta^2) \sum (x^2)}{(n-2) [n \sum (x^2) - (\sum x)^2]} \right\}^{1/2} \quad (137)$$

The numerical value of α_c was estimated to be ± 3.6 μ -coulombs cm^{-2} and is shown in dotted straight lines on both sides of the line for q_+ . It will be noted that q_+ or Γ_{K^+} is close to zero at potentials positive to the e.c.m. potential, whereas at negative potentials with respect to the e.c.m. potential, Γ_{K^+} is about $+1.0$ μ -coulombs cm^{-2} . The values of $F \Gamma_{Na^+}$ for a solution of 0.3 M sodium chloride evaluated by Grahame¹⁹ have been plotted in Figure XXXIX for comparison; Γ_{K^+} in the organic adsorbate solution is significantly lower than Γ_{Na^+} , a result which suggests that upon addition of the neutral organic adsorbate, which is specifically adsorbed at mercury, preferential adsorption of pyridine results in a diminished adsorption of K^+ ions. In the neutral adsorbate solutions, the ionic charge in the double layer thus appears to be displaced, while in the case of ionic organic adsorbates the simple ionic charge in the double layer appears to be replaced by the organic ion charge, as we have observed in the discussion of q_s values previously (see page /88).

D. THE ESIN AND MARKOV EFFECT²⁷

(1) Introductory

A general account of the "Esin and Markov Effect" has

been presented in Chapter I of this thesis. Further qualitative discussion of the change of the potential of the e.c.m. with respect to changes in log concentration of the neutral organic molecules and their conjugate ions has been given on pages 152 and 182 respectively (see Figure XX page 153 and Figure XXVIII page 185). The earlier brief presentation was given primarily to confirm the hypothesis of orientation of the neutral molecules and also to emphasise the different adsorption behaviour observed with varying molecular structures, in particular the availability of π -electrons in the adsorbate molecule or the corresponding ion.

It may be recalled that the Esin and Markov Effect referred specifically to the fact that $E^{e.c.m.}$ was a linear function of the logarithm of the concentration for aqueous electrolytes. Mention has also been made of Parson's discussion of the Esin and Markov Effect from a thermodynamic standpoint;³⁶ his results indicate that the effect may be obtained not only at the e.c.m., but at any point on the electrocapillary curve. The important question arises whether there exists an Esin and Markov Effect for neutral molecules in the same way as it does for the ions and how such an effect might be treated. This matter (not previously investigated) necessitates a more thorough investigation before the above query can be answered. A suitable method of examination would be to apply

the equation derived by Parsons for ions to the data obtained in the present work, and to make a comparative test for un-ionised molecules by applying to the appropriate experimental data an analogous equation derived thermodynamically for neutral molecules.

(11) Thermodynamic Analysis of the Esin and Markov Effect for Ionic Systems and Applications to the Experimental Data

Following Parsons,³⁶ we can write the Gibbs-Lippmann electrocapillary equation at constant temperature and pressure in the form:

$$-d\gamma = q_M dE^\pm + \Gamma_\mp d\mu \quad (138)$$

where the symbols have their usual significance. Since equation (138) is an exact differential, the following differential relationship may be obtained by standard methods

$$\left(\frac{\partial E^\pm}{\partial \mu} \right)_{q_M} = - \left(\frac{\partial \Gamma_\mp}{\partial q_M} \right)_\mu \quad (139)$$

Equation (139) can be written in terms of $q_\mp$, the charge in the solution due to anions or cations as

$$\left(\frac{\partial E^\pm}{\partial \ln a_s} \right)_{q_M} = - \left(\frac{2RT}{Z_\mp e} \right) \left(\frac{\partial q_\mp}{\partial q_M} \right)_{a_\pm} \quad (140)$$

where a_s is the mean activity of the salt. In applying this equation derived by Parsons to our system where specifically

adsorbed cations are involved, we must rewrite (140) in the following form:

$$\left(\frac{\partial E^-}{\partial \ln a_+} \right)_{q_M} = - \frac{RT}{F} \left(\frac{\partial q_{\text{specific}}}{\partial q_M} \right)_{a_+} \quad (141)$$

where q_{specific} now represents q_+ the charge due to the cation, and a_+ (the activity for the cation) has been assumed to be equivalent to a_s (i.e. a_+) since the activity of Cl^- ions in the electrolyte will be almost invariant in the solutions studied which always contained excess HCl.

The experimental data for pyridinium⁺, 2-amino-pyridinium⁺, piperidinium⁺ and anilinium⁺ ions have been used to examine the applicability of equation (141). Values of q_{specific} (assumed equal to $F \Gamma_A$) were plotted against q_M (both computed at constant activity of the organic electrolyte) from data obtained from four electrocapillary curves for each of the above-mentioned ions. The slopes $(\partial q_{\text{specific}} / \partial q_M)_{a_+}$ were then evaluated (see Figures XL a, XLI a, XLII a and XLIII a pages 216-219).

Correspondingly, values of E^- (the potential of the electrode with respect to the potential of the calomel reference electrode) and $\frac{RT}{F} \ln a_+$ (assuming $a_+ = a_s$) at a chosen constant value of q_M (at the e.c.m.), were plotted for the four organic cations, and the slopes evaluated (see Figures XL b, XLI b, XLII b and XLIII b, Pages 216-219). For convenience, the

Figure XL:

Pyridinium⁺ (Esin and Markov Effect)

- a) Plots of q_{specific} vs q_M at constant a_+
- b) Plot of E^- vs $\frac{RT}{F} \ln a_+$ at constant q_M

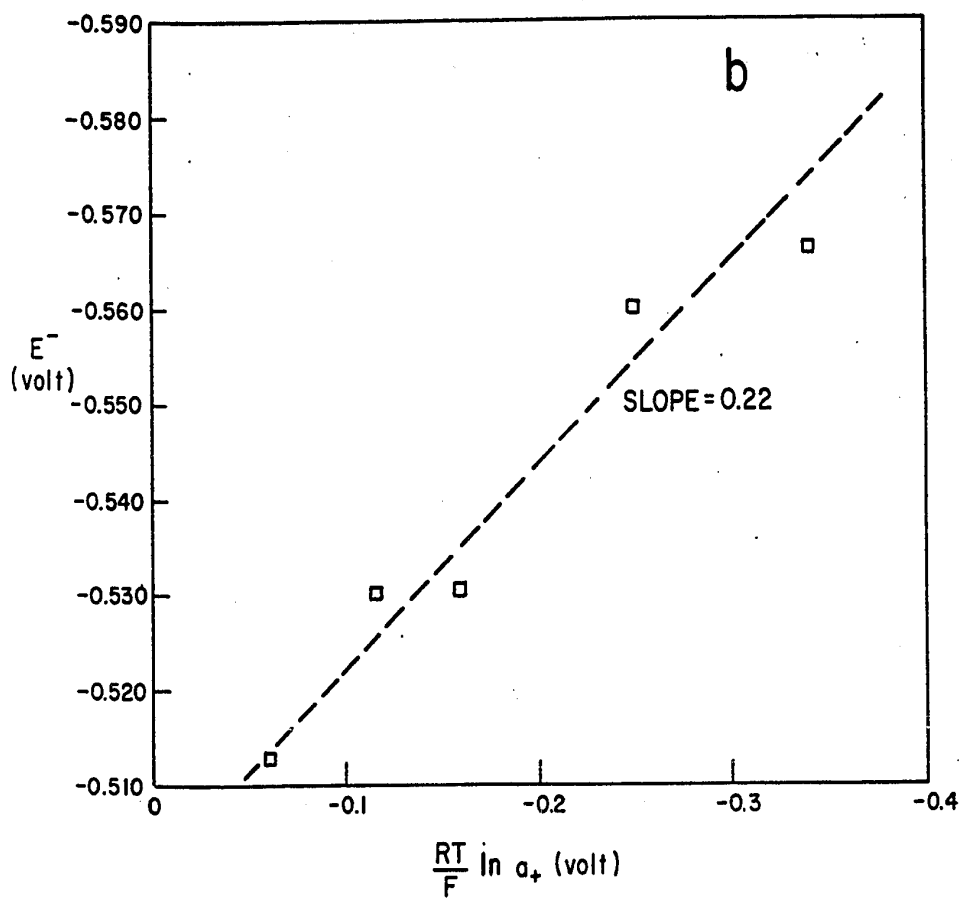
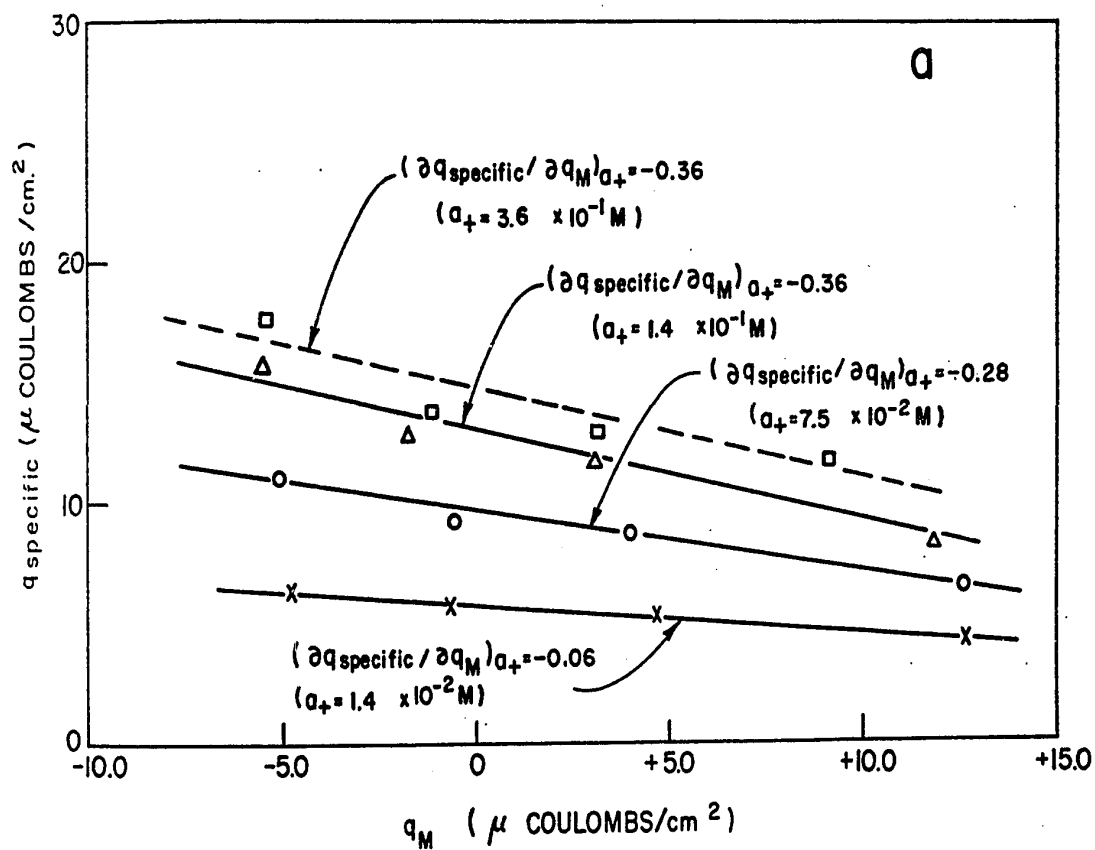


Figure XLI:

2-Aminopyridinium⁺ (Esin and Markov Effect)

a) Plots of q_{specific} vs q_M at constant a_+

b) Plot of E^- vs $\frac{RT}{F} \ln a_{+}$ at constant q_M

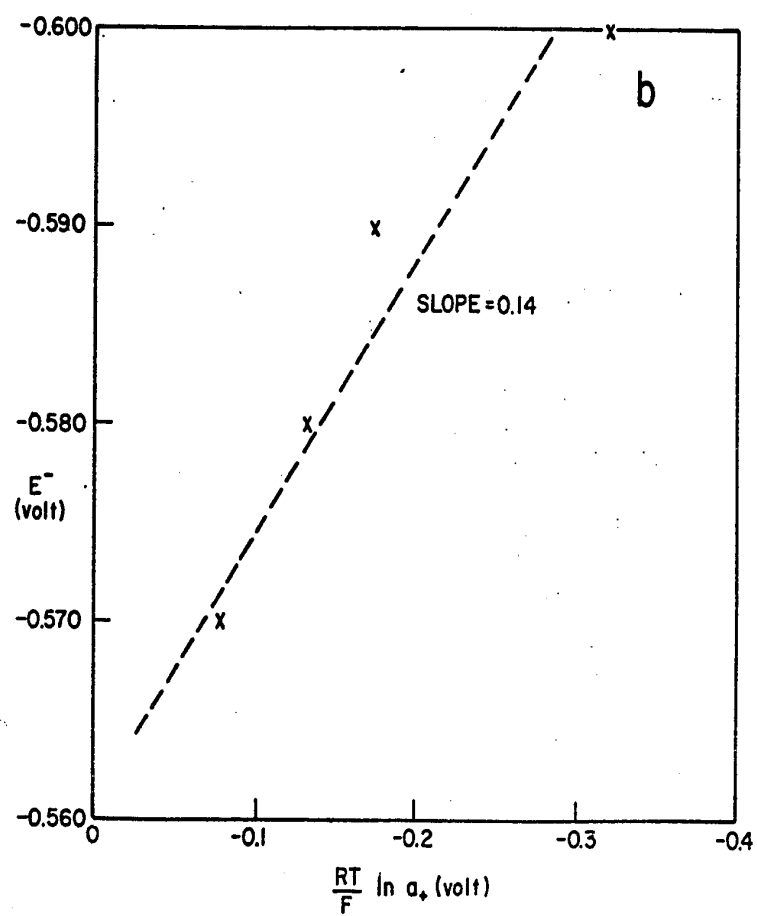
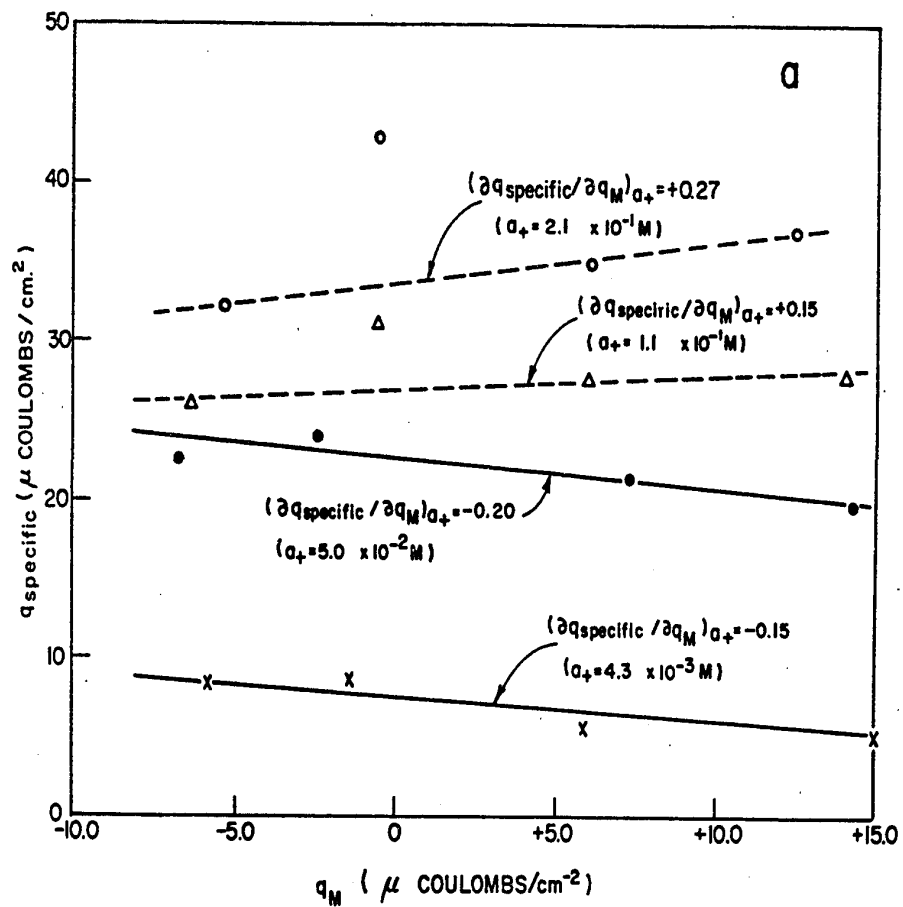


Figure XLII:

Piperidinium⁺ (Esin and Markov Effect)

- a) Plots of q_{specific} vs q_M at constant a_+
- b) Plot of E^- vs $\frac{RT}{F} \ln a_+$ at constant q_M

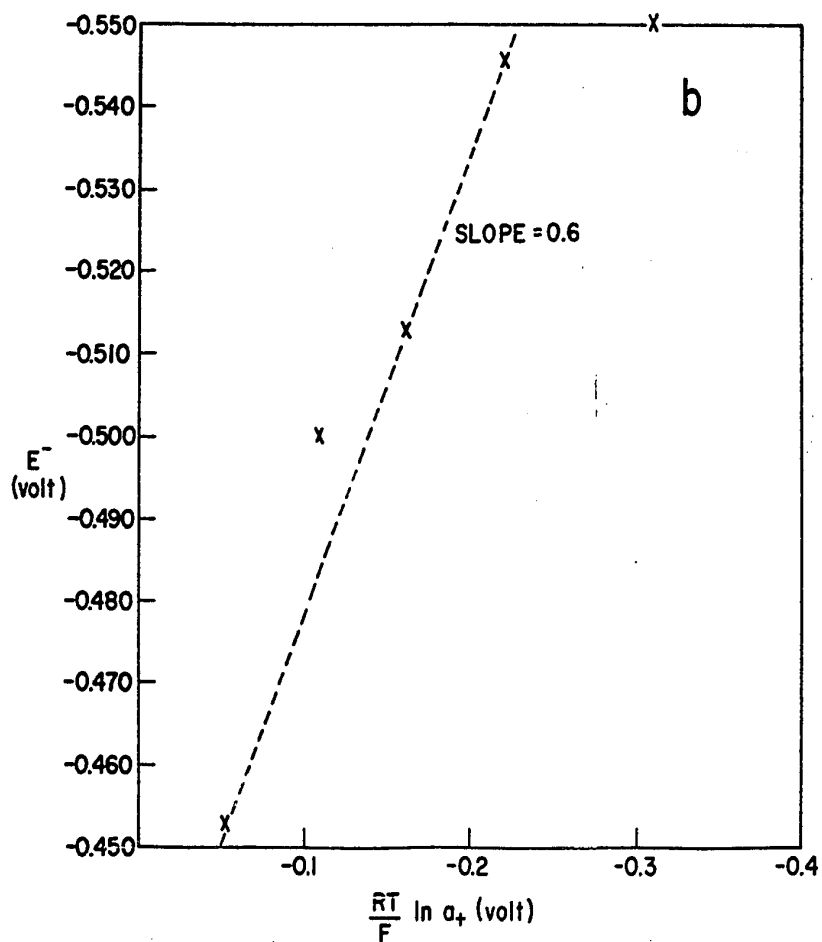
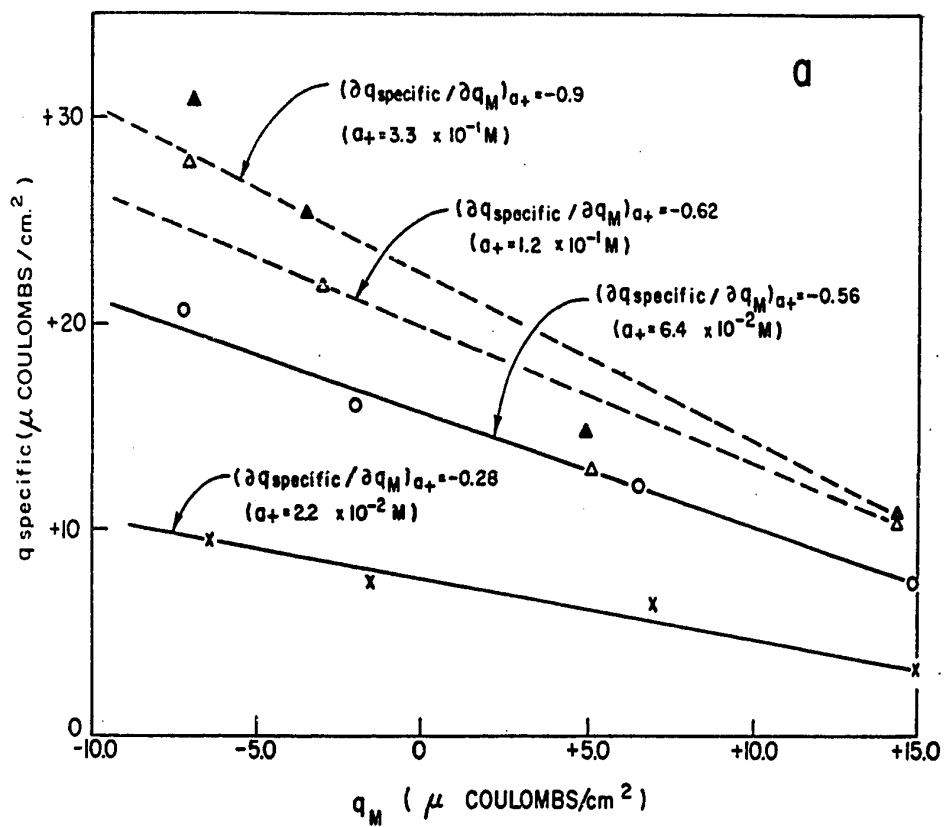
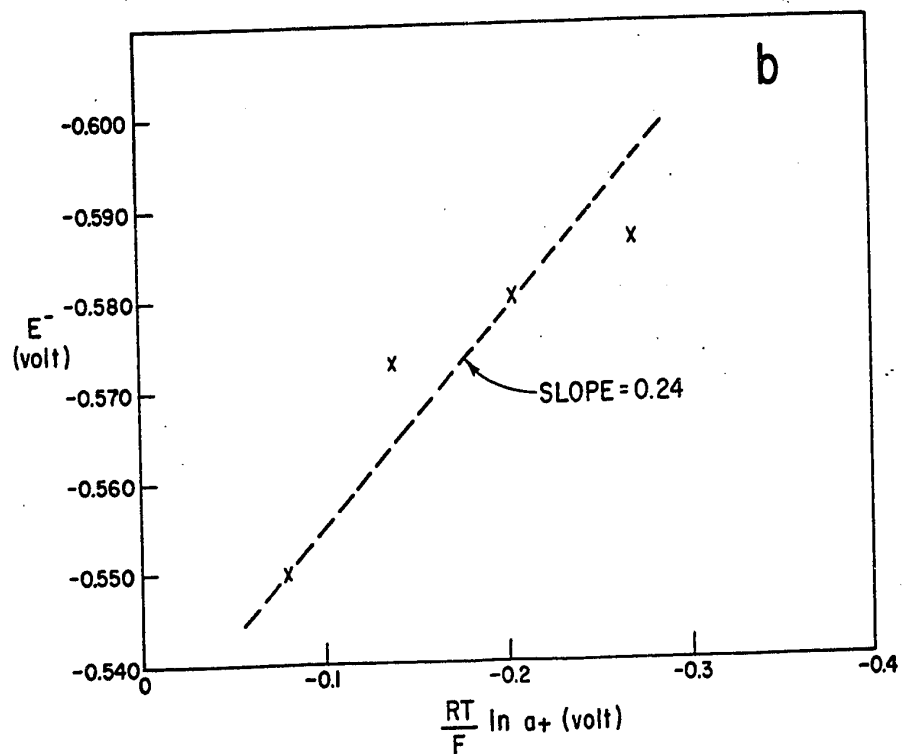
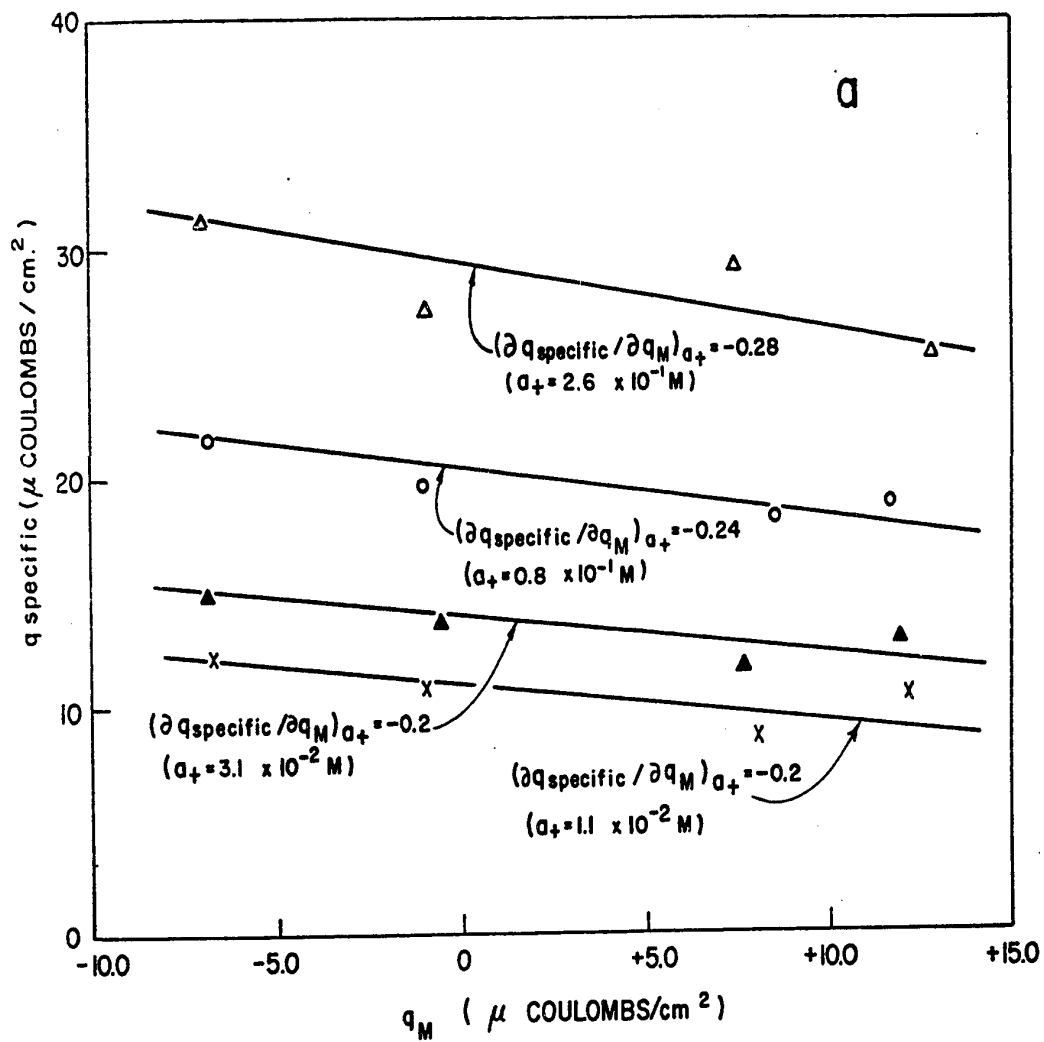


Figure XLIII:

Anilinium⁺ (Esin and Markov Effect)

- a) Plots of q_{specific} vs q_M , at constant a_+
- b) Plot of E' vs $\frac{RT}{F} \ln a_+$, at constant q_M .



results of these derived calculations are summarised in Table X (page 221). It is noteworthy that within the limits of experimental error, the values of $(\partial q_{\text{specific}} / \partial q_M)_{a_+}$ are in satisfactory agreement with those of $(\partial E / \frac{RT}{F} \partial \ln a_+)_{q_M}$ as required theoretically.

(iii) Thermodynamic Analysis of the Esin and Markov Effect for Neutral Molecules and the Application to Experimental Data

Inspection of the electrocapillary curves (q.v. Chapter III) for neutral organic molecules in potassium chloride solutions indicates that the potential at the electrocapillary maximum changes with variation in concentration of the organic substrate. This provides adequate grounds for supposing that there may be an "Esin and Markov Effect" for neutral molecules, although the actual quantitative change in $E^{\text{e.c.m.}}$ with changes in the logarithm of concentration or activity may not necessarily be similar in magnitude to that observed for ions. Therefore, a comparable new thermodynamical equation for un-ionised molecules, equivalent to that deduced by Parsons for ions, may be derived for describing the "Esin and Markov" behaviour of neutral molecules.

Thus, we write equation (139) for neutral molecules (A) in the following way

$$\left(\frac{\partial E_{\text{cal}}}{\partial \mu_A} \right)_{q_M} = - \left(\frac{\partial \Gamma_A}{\partial q_M} \right)_{\mu_A} \quad (142)$$

where E_{cal} is the same as E° in equation (139). Equation (142) may obviously be rewritten as

$$\left(\frac{\partial E_{\text{cal}}}{\partial \ln a_A} \right)_{q_M} = RT \left(\frac{\partial \Gamma_A}{\partial q_M} \right)_{\mu_A} \quad (143)$$

where a_A is the activity of the neutral molecule. As shown previously, we can test an equation such as (143) by plotting (1) E_{cal} versus $RT \ln a_A$, at constant q_M (e.g. at the e.c.m.) and (2) Γ_A versus q_M , at constant a_A for pyridine^o, 2-aminopyridine^o, piperidine^o and aniline^o (the superscript "o" indicates the neutral molecule). The slopes of both sets of curves for the four organic compounds were evaluated and are compared in Table XI (page 223). The graphical plots denoted above by (1) and (2) are illustrated in Figures XLIV (a) to XLVII (a) and XLIV (b) to XLVII (b) on pages 224-227.

It may be noted that the curves of E_{cal} versus $RT \ln a_A$, at constant q_M , for pyridine and piperidine do not show changes of slope over the range of activities examined. Aniline and 2-aminopyridine demonstrate a change of slope over the range of activities investigated. This is consistent with the plots of $\Delta E^{\text{e.c.m.}}$ versus $\log c$ as shown in Figure XX page 153. In contrast these changes of slope do not occur

TABLE XI

Test of equation (143) for the Esin and Markov

Effect due to neutral organic molecules

System	a_A	$(\partial \pi_A / \partial q_M)_{a_A}$	$(-\partial E_{cal}/RT \partial \ln a_A)_{q_M}$
Pyridine ° in N KCl	$6.29 \times 10^{-1}M$	-1.9×10^{-5}	-1.8×10^{-5}
	$3.15 \times 10^{-1}M$	-2.1×10^{-5}	
	$1.18 \times 10^{-1}M$	-1.3×10^{-5}	
	$2.35 \times 10^{-2}M$	-1.4×10^{-5}	
2-Amino- Pyridine in N KCl	$2.92 \times 10^{-1}M$	-2.4×10^{-5}	-3.1×10^{-5}
	$1.17 \times 10^{-1}M$	-0.8×10^{-5}	
	$3.05 \times 10^{-2}M$	-0.3×10^{-5}	
	$0.872 \times 10^{-2}M$	-0.1×10^{-5}	
Piperidine ° in N KCl	$3.98 \times 10^{-1}M$	Solid line -5.8×10^{-5}	Dotted line -1.6×10^{-5}
	$1.50 \times 10^{-1}M$	-8.0×10^{-5}	-0.8×10^{-5}
	$6.12 \times 10^{-2}M$	-2.7×10^{-5}	-0.5×10^{-5}
	$2.27 \times 10^{-2}M$	-0.8×10^{-5}	-0.3×10^{-5}
		Average: -4.3×10^{-5} ($\pm 2.6 \times 10^{-5}$)	Average: -0.8×10^{-5} ($\pm 0.04 \times 10^{-5}$)
		Average for dotted solid lines -2.6×10^{-5}	
			3.3×10^{-5}
Aniline ° in N KCl	$1.70 \times 10^{-1}M$	-3.1×10^{-5}	0.8×10^{-5}
	$7.85 \times 10^{-2}M$	-1.7×10^{-5}	
	$2.70 \times 10^{-2}M$	-0.55×10^{-5}	
	$6.30 \times 10^{-3}M$	-0.10×10^{-5}	

The figures in the third and fourth columns are probably significant to the first decimal place.

Figure XLIV:

Pyridine^o (Esin and Markov Effect)

- a) Plots of γ_A vs q_M at constant a_A
- b) Plot of E_{cal} vs $RT \ln a_A$ at constant q_M

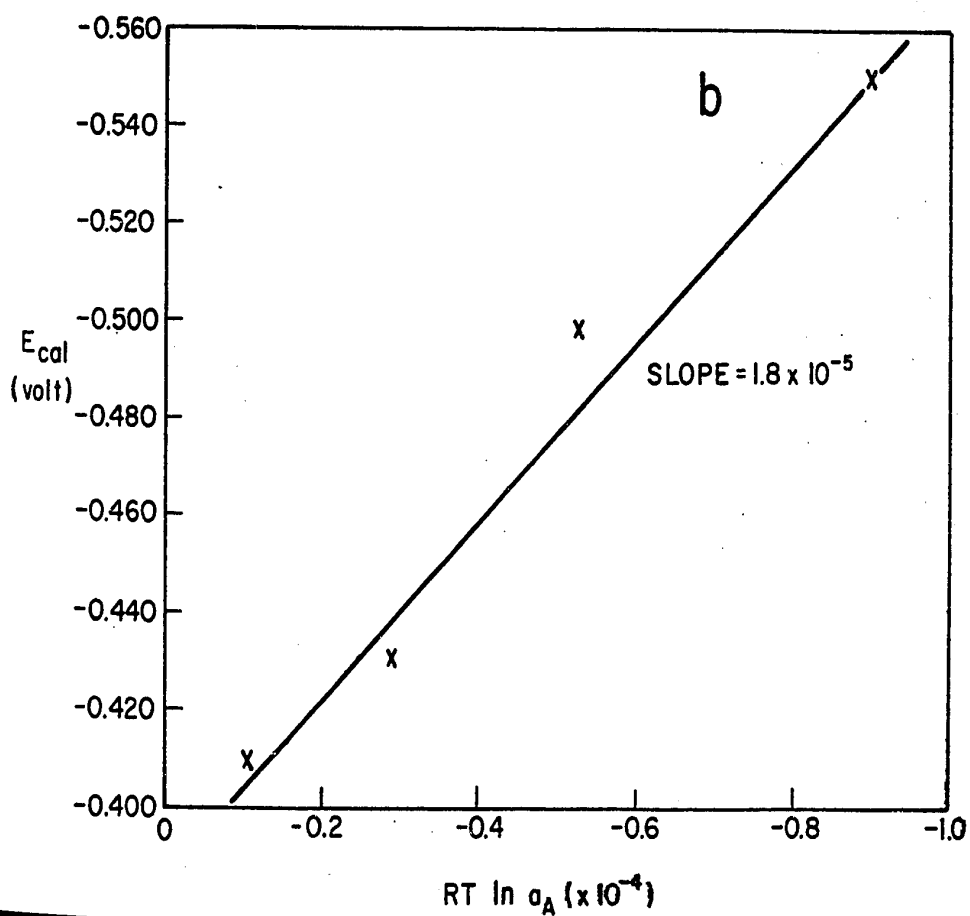
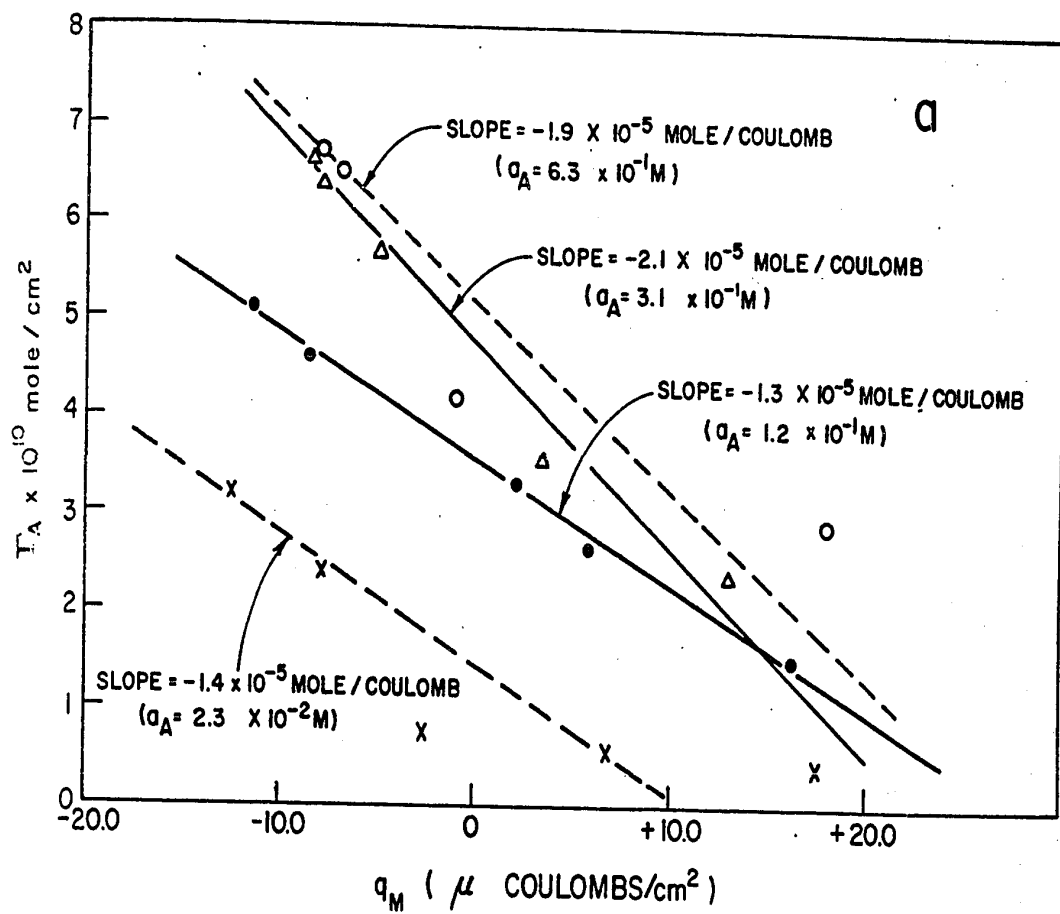


Figure XLV:

2-Aminopyridine⁰ (Esin and Markov Effect)

a) Plots of $\sqrt{I_A}$ vs q_M at constant a_A

b) Plot of E_{cal} vs $RT \ln a_A$ at constant q_M

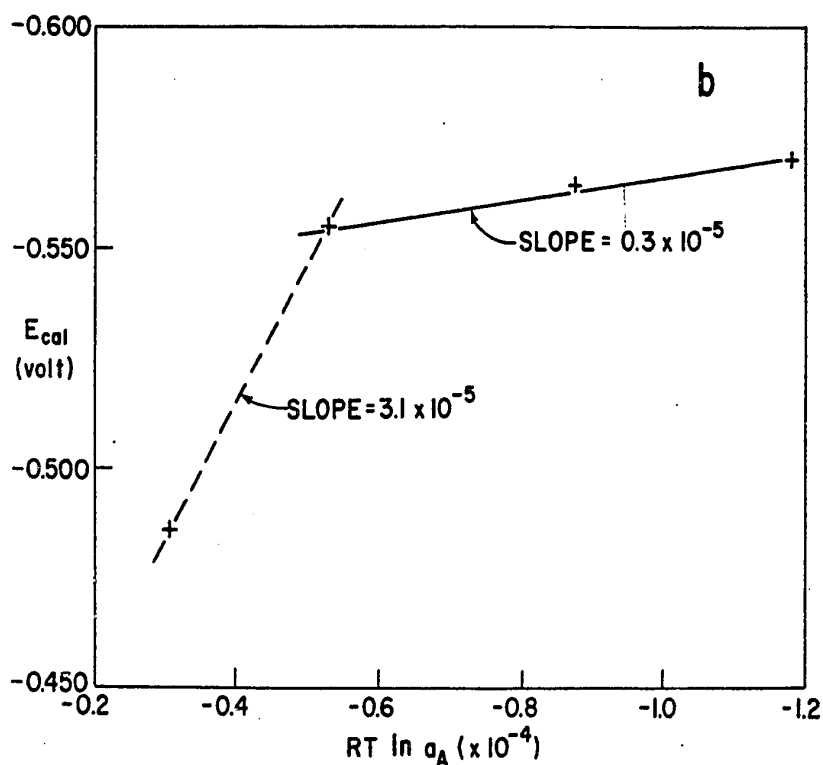
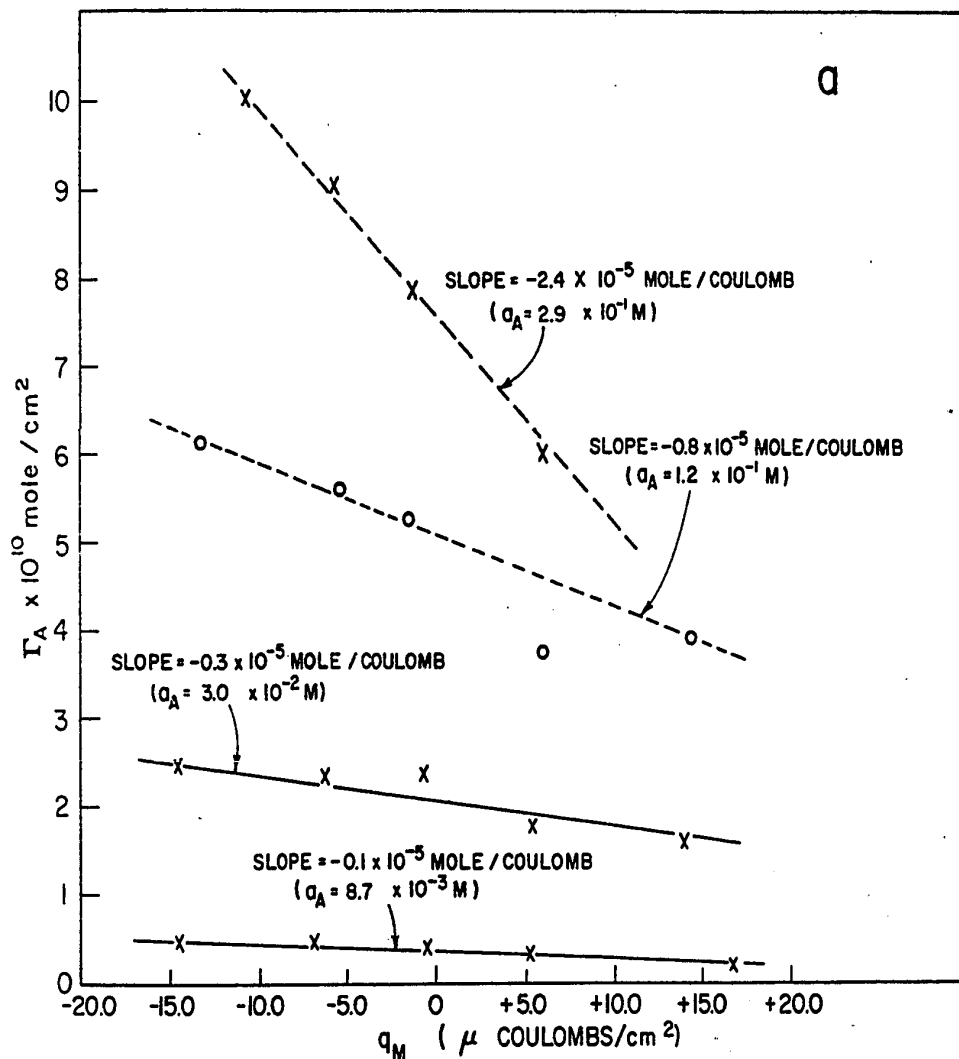


Figure XLVI:

Piperidine^o (Esin and Markov Effect)

- a) Plots of Γ_A vs q_M , at constant a_A
- b) Plot of E_{cal} vs $RT \ln a_A$, at constant q_M .

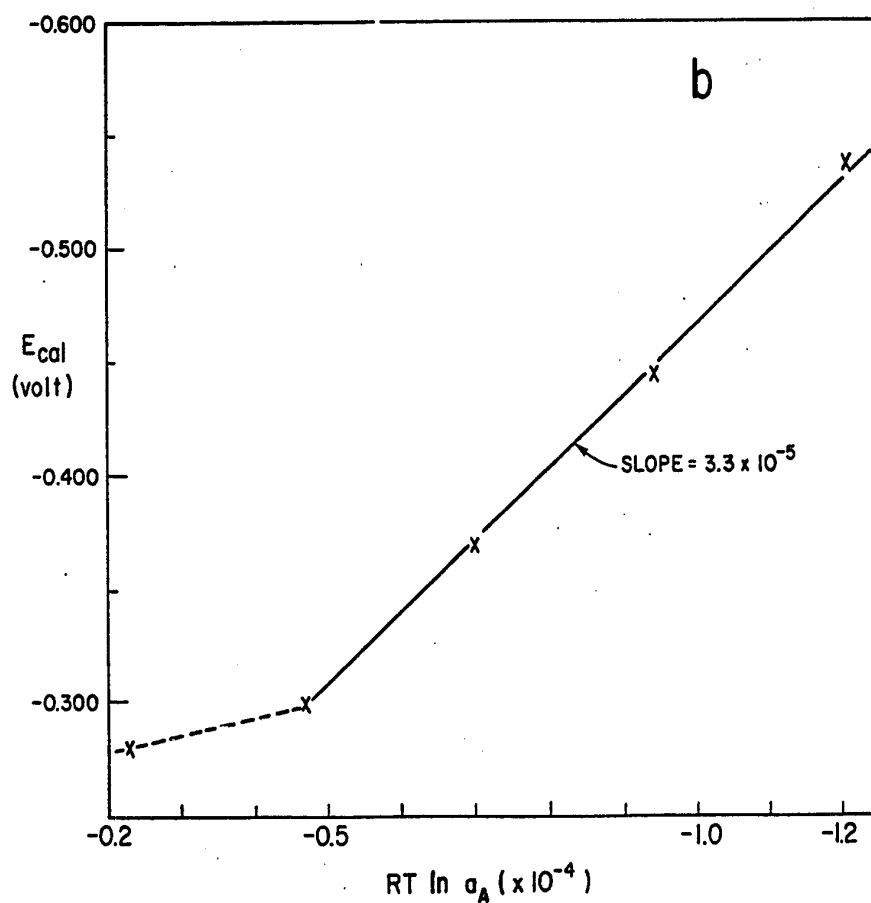
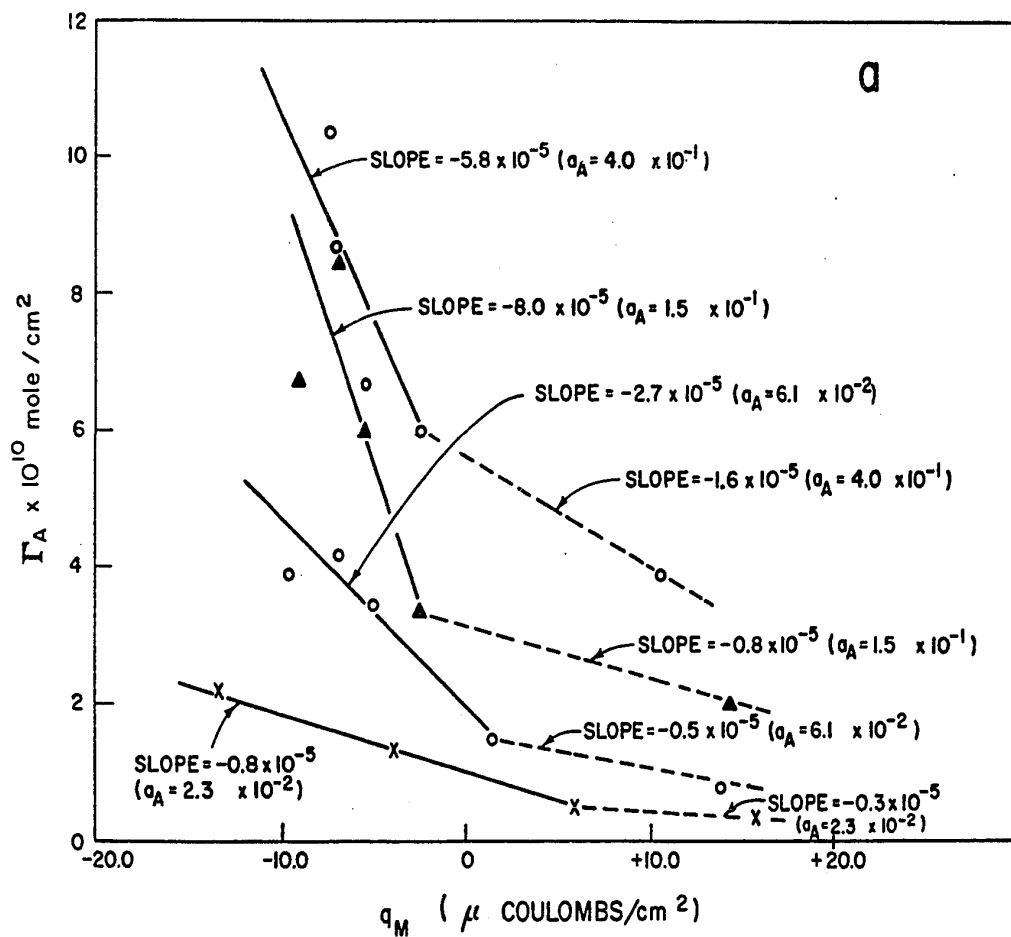


Figure XLVII:

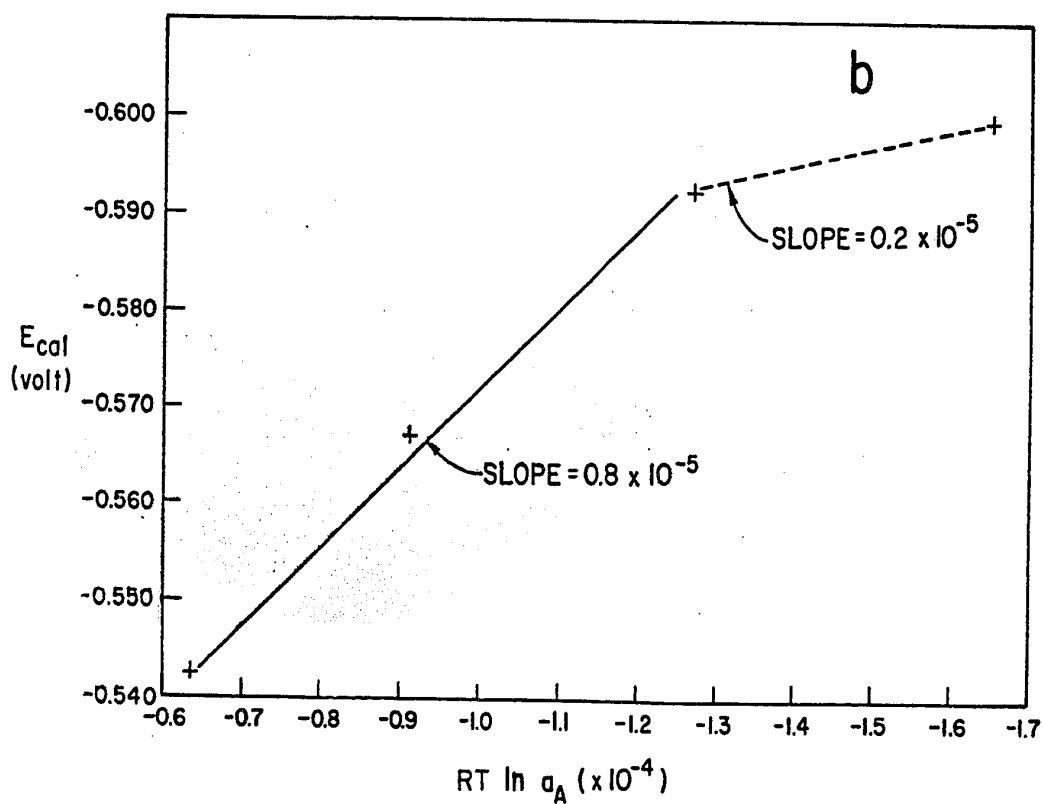
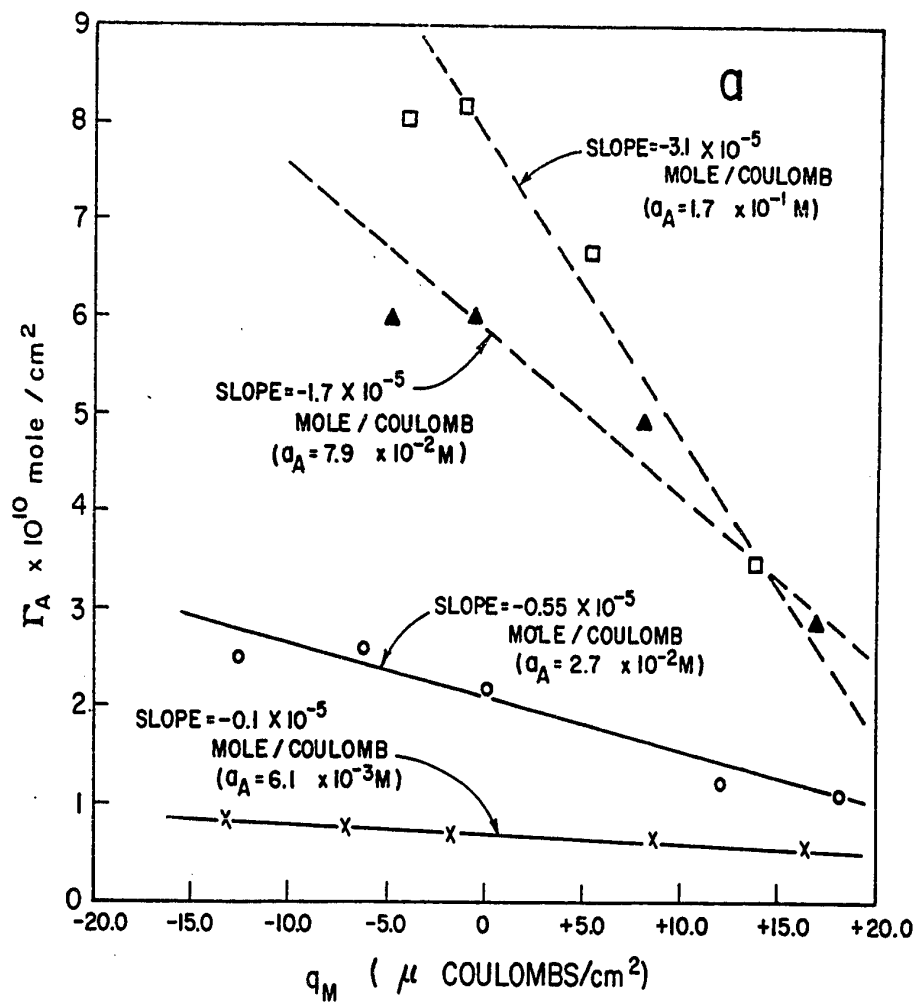
Aniline^o (Esin and Markov Effect)

- a) Plots of $\overline{f}_A$ vs q_M at constant a_A
- b) Plot of E_{cal} vs $RT \ln a_A$ at constant q_M

Figure XLVII:

Aniline^o (Esin and Markov Effect)

- a) Plots of f_A vs q_M , at constant a_A
- b) Plot of E_{cal} vs $RT \ln a_A$, at constant q_M .



in Figures XL (b) to XLIII b, since equivalent plots of $E^{e.c.m.}$ against $\log c$ (Figure XXVIII) page 185) are also linear and without changes of slope.

The comparison of the evaluated slopes, $(\partial \Gamma_A / \partial q_M)_{a_A}$ and $(\partial E_{cal} / RT \partial \ln a_A)_{q_M}$ in Table XI show that they are generally not in good agreement with one another and the comparison is less satisfactory than for the case of the organic ions. From the data in Table XI it will be seen that $(\partial \Gamma_A / \partial q_M)_{a_A}$, which should be a constant quantity for varying concentrations of A, in fact tends to increase with increasing adsorbate concentration. Tentatively it may be suggested that this variation arises from orientation of the surface layer of adsorbate at high coverages when the adsorbate is present at high concentrations. In those cases where two regions of different slope in the $\Delta E_{e.c.m.} - \log C$ plot can be discerned (see Figure XX), e.g. for aniline or 2-aminopyridine, the slope at higher concentrations is certainly larger than that for lower concentrations and this is also the case for the $(\partial \Gamma_A / \partial q_M)_{a_A}$ values (column 3, Table XI). In these cases therefore there is qualitative consistency between theory and experiment.

Previously ¹⁵⁰ it has been assumed that $\Delta E_{e.c.m.}$ could be expressed in terms of the Helmholtz surface potential

by the relation (cf. p. 152):

$$\Delta E_{e.c.m.} = \frac{4 \pi N \mu \Gamma}{\epsilon_s} \quad (126)$$

where Γ is the surface excess in mole cm^{-2} of the adsorbate of effective surface moment μ in the surface phase of dielectric constant ϵ_s . However, our present results indicate that the slope $d(\Delta E_{e.c.m.})/d\Gamma$ is not simply proportional to μ for the various adsorbates and this may be because other molecular and electronic structure effects (π -orbital interaction with the metal) influence the orientation and hence the moment effective in a direction normal to the surface. It is clear from the foregoing thermodynamic analysis that the previously assumed relationship for $\Delta E_{e.c.m.}$ does not have a thermodynamic basis.

CHAPTER V

PART II: ADSORPTION AT SOLID ELECTRODES

A. INTRODUCTION

Elsewhere (Chapter I) reference has been made to the problem of examination of electrochemically interesting adsorbates at solid metals. Despite the much greater contemporary interest in and more complex electrode kinetic behaviour at solid metals than at mercury, very little information is available on the adsorption of organic molecules and ions at such metals. The effects of such adsorbates are interesting in relation to (a) electrocrystallisation of metals, (b) inhibition of one or both of the partial processes in electrochemical corrosion of metals and (c) catalytic effects on the hydrogen evolution reaction.

Previous studies at solid metals have utilised (1) radio-tracer procedures¹⁹³⁻¹⁹⁵ but these are for the most part inapplicable for organic solutes except when irreversible adsorption occurs (and non-equilibrium conditions prevail), or (2) electrode capacity determinations; the interpretation of the latter measurements is complicated by frequency variation of the capacity at solid metals, and in any case can only give non-thermodynamic data on adsorption since the integration constants required for calculation of data by this method

could only be obtained by electrocapillary measurements, which are of course impossible at solid metals (q.v. Chapter I).

B. EXPERIMENTAL

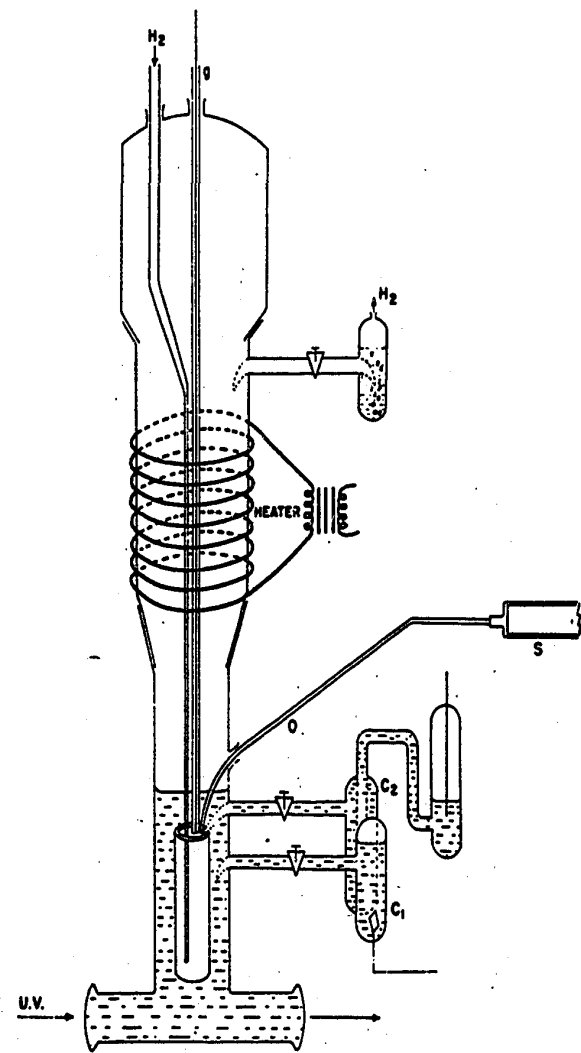
(1) Apparatus

A direct spectrophotometric method has been developed for determination of adsorption of suitable light-absorbing organic and inorganic ions and molecules at solid metals under thermodynamically reversible conditions. An apparatus (see Figure XLVIII page 232) was constructed to enable adsorption studies to be made by following directly and continuously the change of ultraviolet extinction of solutions of suitable organic compounds in an electrochemical cell containing an electrode on which the adsorption was to be studied.

The first electrochemical cell developed in this work was made of pyrex glass and sealed to a special ~~quartz~~ optical cell which could be placed in the light beam in the cell-holder compartment of a Beckmann D.K. 2 recording spectrophotometer. A calibrated micrometer burette which could be read to 0.0005 ml was inserted through an upper tube in the cell and delivered known amounts of a solution of previously determined concentration into the apparatus containing the electrode. The solution was stirred by passing a stream of purified hydrogen, helium, or nitrogen. In the case of hydrogen, it was experimentally ascertained that the gas did not

Figure XLVIII:

Side view of the first experimental cell used for
the determination of adsorption at solid electrodes.

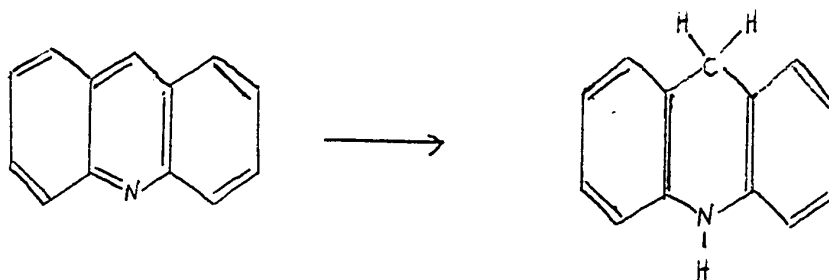


SIDE VIEW OF THE EXPERIMENTAL CELL

catalytically reduce the chosen adsorbate molecules or ions in the presence of the metal.

(ii) Preliminary Experiments¹⁹⁶

Exploratory experiments were made with acridine on copper electrodes made of high purity copper foil and having an area of 100 cm^2 . The electrodes were coiled in the form of cylindrical helices to present as much area to as little volume of solution as possible. In acid solutions, traces of cuprous ions appeared in the solution due to dissolution of the copper, presumably of account of residual oxygen being present. These ions interfere with the spectrophotometric determination of the acridine, since they absorb in the same wavelength region as does acridine. Use of "oxygen free" solutions was later shown to diminish the interference by traces of copper ions. With silver foil electrodes, no metal ions could be detected spectrophotometrically, but the application of cathodic potentials (relative to the hydrogen electrode in the same solution) causes reduction of acridine to acridan (5,10-dihydroacridine):



Although this effect interferes with the determination of acridine adsorption, it provides a useful way of following the electrochemical reduction of acridine and the concentration of its reduced form can be followed. The concentrations of both substances can hence be measured simultaneously. With quinoline on silver electrodes, adsorption could be detected at high negative potentials, but some cathodic reduction occurred. However it was with silver that the first indication was obtained that the method could in principle be successfully used. With the 100 cm² electrodes used in the preliminary work, adsorption could be observed qualitatively by a decrease of ultraviolet absorption of the solution but the effect was too small to be measured accurately.

(iii) Development of the Method

The essential points of the preliminary work done by Mr. Zadwizki were repeated and confirmed by the present author. The work indicated that it would be possible to study the adsorption of quinoline and acridine if all interferences were eliminated, and also if the sensitivity of the method could be improved. It was clear that the method was sound in principle, but that it required more elaborate and rigorous purification techniques and probably the introduction of other refinements. Further work was carried out in which no net current was passed. These experiments were done to test the

value of the method. Firstly, the adsorption of acridine on silver in neutral aqueous solutions was determined, and the reproducibility was found to be within 5-10% with replicate determinations. Experiments were concurrently performed on copper in neutral and alkaline solutions (N/10 sodium carbonate) of acridine.

It was then considered that the best method of approach was to extend the experiments on silver by operating over a wider range of concentrations of acridine solutions. This was limited by the volume of solution which could be used for the subsequent ultraviolet absorbance measurements and the relative changes of absorbance which could be detected. High concentrations of acridine solution were also ruled out owing to the strongly fluorescent nature of the material, which did not permit its absorbance to be satisfactorily measured by the spectrophotometer. Various unsuccessful and time-consuming artifices were devised to increase the change in concentration of acridine due to its adsorption on silver, or on any of the following metals: nickel, tungsten, copper or iron. These failures led to the development of electrodes of increased surface area.

(iv) Final successful Technique

High purity 100 x 100 mesh wire gauze electrodes of copper, nickel, and silver having an apparent geometric area of 700 cm^2 , calculated from the mesh number, the diameter of

the wire threads and the over-all size of gauze sample taken, were made up by rolling the gauze into a cylindrical helix. This could be immersed in only 15 ml. of the adsorbate solution, whose ultraviolet absorbance had been determined prior to immersion of the electrode in a newly constructed combined electrochemical - optical cell (see Figure XLIX page 237). The apparatus was, in principle, similar to that shown in Figure XLVIII and was designed to be used with a D.U. model spectrophotometer using a 1 cm path-length cell. Changes in ultraviolet absorbance of the solution (up to 70% of the initial values) due to removal of the adsorbate by adsorption on the electrode could then be measured directly by means of the spectrophotometer. Figure L page 238 illustrates an example of the recorded change in absorbance of an acridine solution due to adsorption by copper. In this figure the absorbance of two standard solutions (std. 1 and std. 2) of different concentrations (within the range stated below) are compared with the absorbances of corresponding solutions after equilibrium adsorption had been attained. Data for 2 samples at each concentration are shown and illustrate the reproducibility of the results. The measurements could be made with an accuracy of 1% over a concentration range of 5×10^{-7} to 1×10^{-4} M depending on the extinction coefficient of the adsorbate and the path length of the optical cell used. The solution can be

Figure XLIX:

Later apparatus designed for measuring adsorption at
solid electrodes.

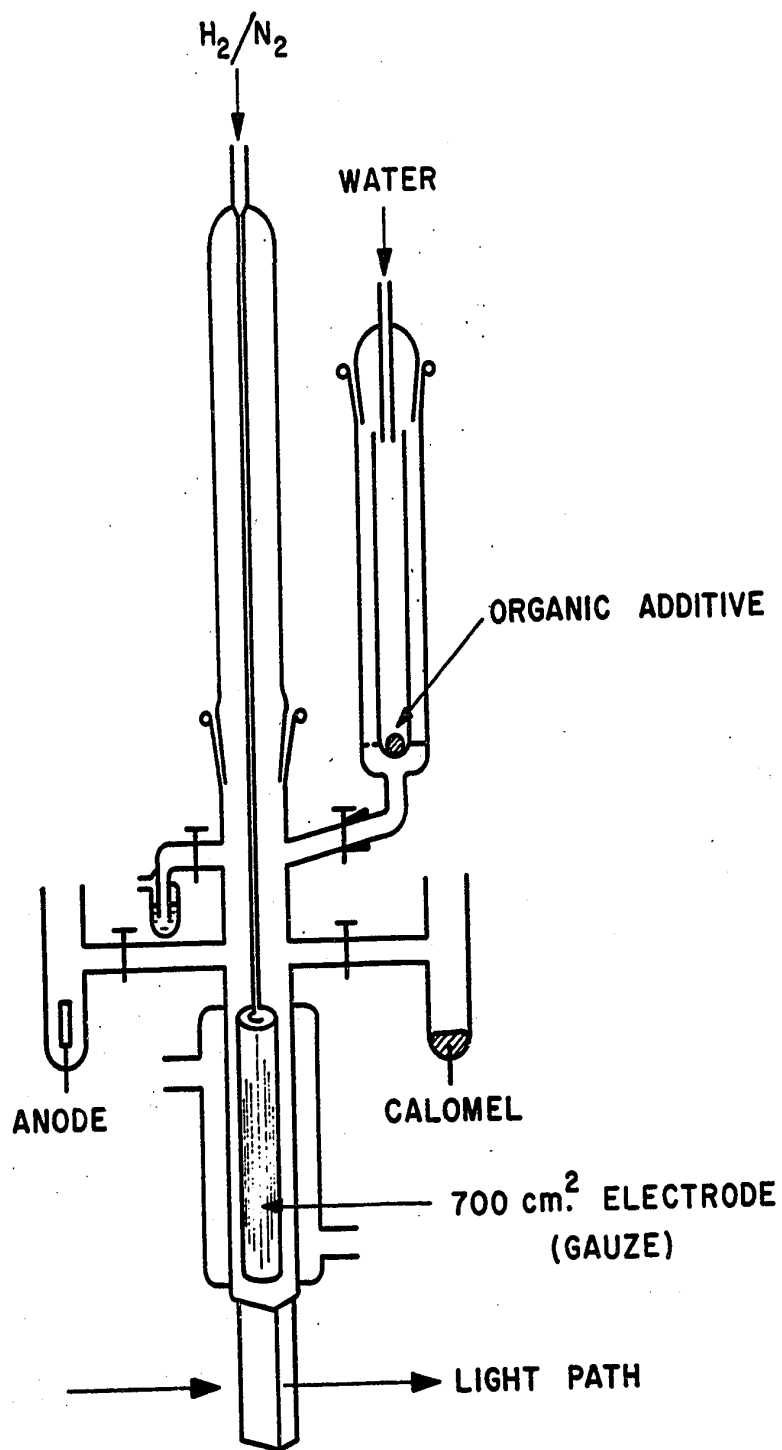
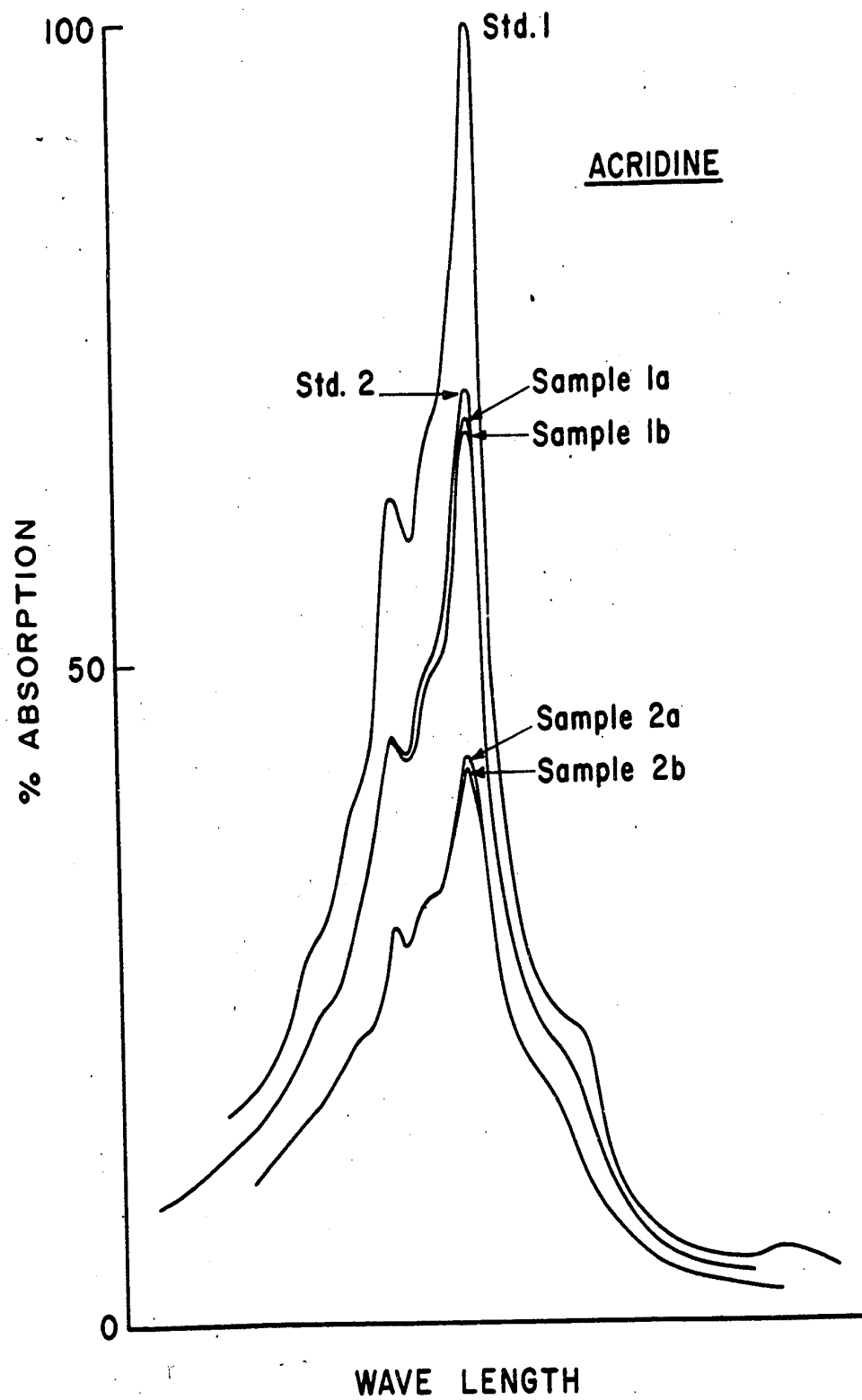


Figure L:

Comparison of the absorbances two standard solutions of acridine at different concentrations (standard 1 and 2) with the absorbances of corresponding solutions after equilibrium adsorption had been attained.



mixed either by passing a stream of purified hydrogen or by manually inverting the apparatus several times. The present system was not made to measure rates of adsorption but some information can be obtained from the data obtained. It was found that equilibrium adsorption occurred in less than 5 minutes after contact of the solution with the metal, most of the adsorption having occurred before measurements could be taken. Solutions containing the electrodes for as long as one hour or more showed very little or no additional change in concentration. The reversibility of adsorption at the solid electrode was ascertained by washing the adsorbate off the electrode surface with water. The same electrode was then immersed in a fresh solution of the substrate when a further quantity (comparable with the first) of the organic adsorbate was removed from the solution.

With neutral solutions the most promising results were obtained by measuring the adsorption of acridine on copper. The choice of nickel as an adsorbent was guided by the strong chemisorptive properties of this metal. The results however were not as expected. Nickel did adsorb measurable amounts of acridine from neutral aqueous solutions but the amounts were small compared with those observed at copper. Dilute acidic and alkaline (N/100 HCl and N/100 Na₂CO₃) solutions of acridine were also examined with nickel, but the presence of

dissolved nickel ions in solution, which have a strong ultra-violet extinction in the experimental wave length region masked the usual absorption peaks due to acridine. The amount of acridine adsorbed on silver from neutral aqueous solutions was of the same order of magnitude as that on nickel.

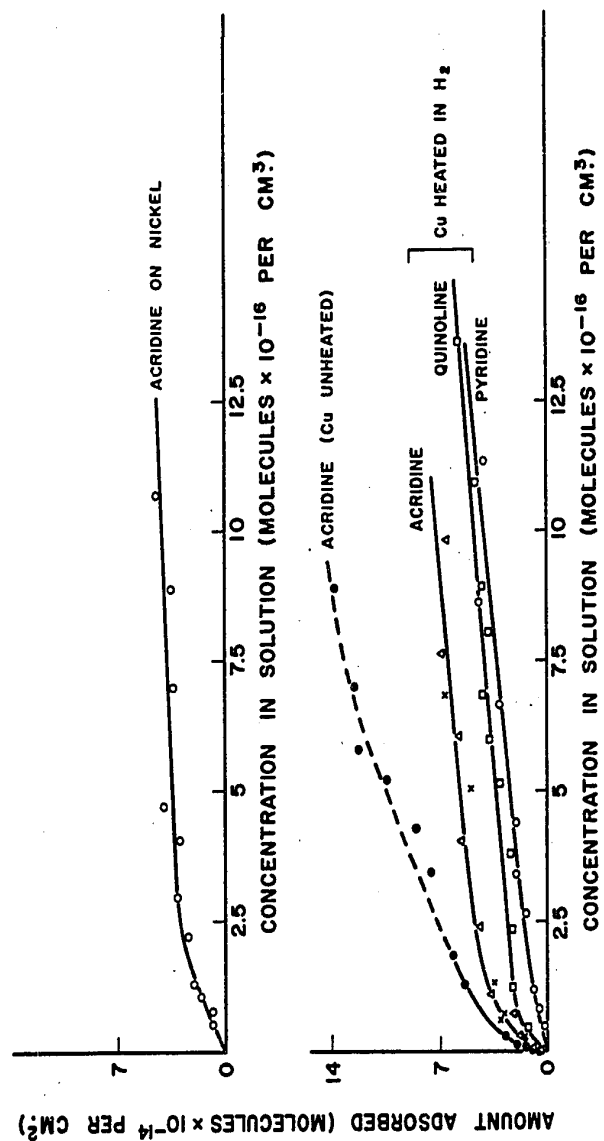
For the above reasons, attention was then focussed on the use of fine copper gauze for further experimentation. Here it was repeatedly found that amounts up to 70% withdrawal of acridine from solution were recorded. This success, in conjunction with the complete absence of any absorption peaks due to acridan, led to the conclusion that acridine was quite definitely absorbed by copper, and that such adsorption could be measured with comparative ease and good reproducibility if standardisation of preparation of the metal surface and other experimental procedures were adopted. A range of concentrations of acridine solutions was used, and a plot of concentration of solute present at equilibrium versus amount adsorbed revealed a curve having the form of an isotherm (see Figure LI, page 241). The reproducibility obtained at first was fair but not excellent. This may have been due to contamination of the copper by an oxide film, and such results would have been only of limited value had not more rigorous methods of standardisation of electrode surfaces been made.

(v) Preparation of Electrodes

Originally the electrodes were washed consecutively

Figure LI:

Adsorption isotherms at 25° C for pyridine, quinoline,
and acridine at copper and nickel gauzes.



with warm carbon tetrachloride, acetone, dilute nitric acid (copper, nickel and silver), dilute hydrochloric acid (copper and nickel only), conductance water, ethyl alcohol, acetone, and ether. Since the oxide film was probably responsible for the variation in adsorption measured, it was removed, after the organic solvent and acid cleaning treatment, by heating the metal in a stream of purified hydrogen at not less than 600° C followed by prolonged outgassing at the same temperature in a high vacuum apparatus. This method of purifying the electrode gave more reproducible results, but the hydrogen-treated electrode adsorbed somewhat less acridine than before, presumably owing to sintering of surface irregularities on the metal and removal of any oxide films of substantial thickness or porosity.

(vi) Comparative Study of Two Electrodes Treated by Different Procedures

In order to obtain an isotherm of nine experimental points, nine sets of the apparatus described (see Fig. XLIX) would have to be used at once. Failing this, the time required to obtain a single isotherm would be rather extended because each used cell would have to be washed, dried, and used again for the next concentration. So that these inconveniences might be avoided a comparative study was made of two electrodes of the same metal and having equal areas, which were cleaned

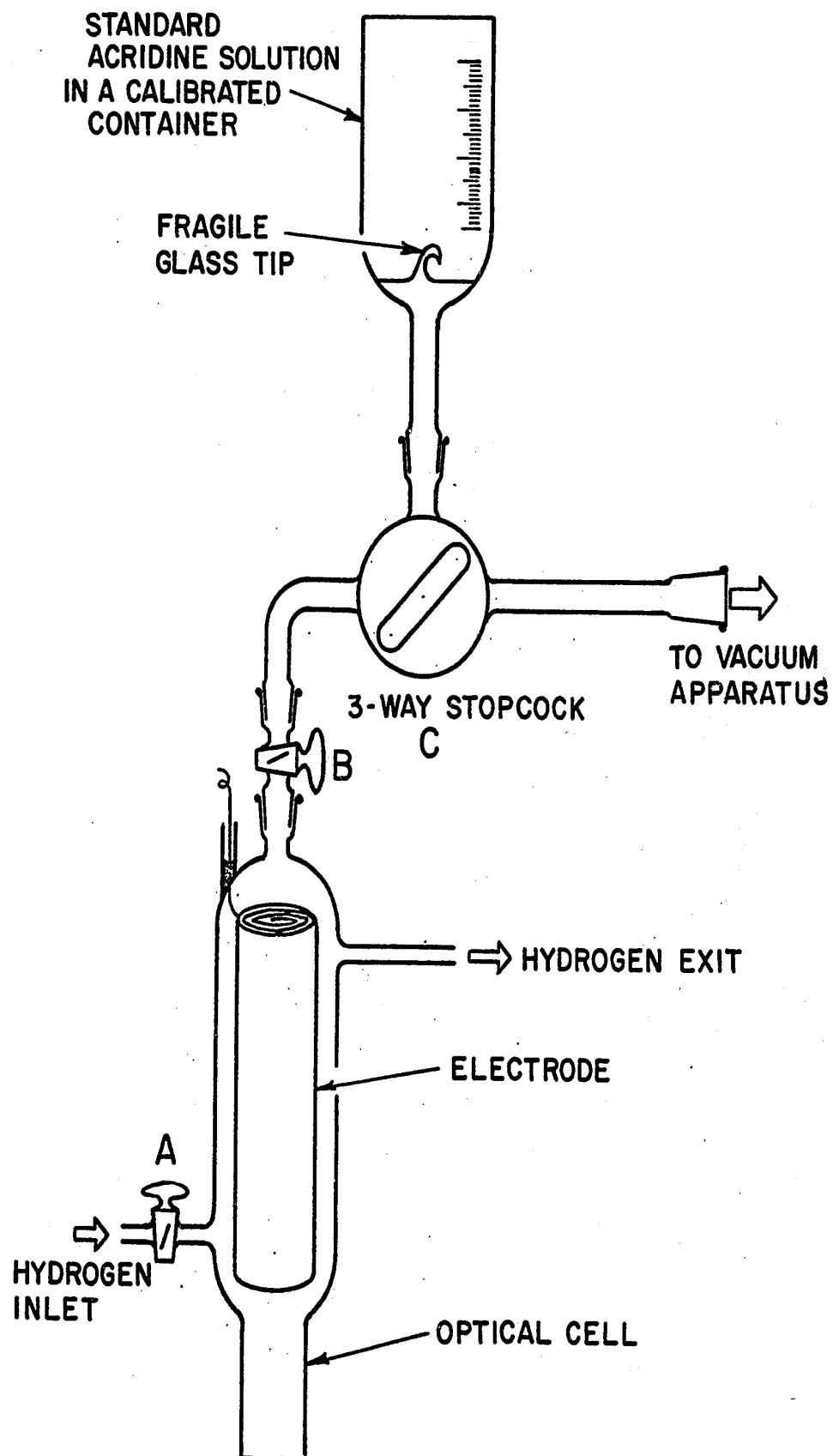
by acids, organic solvents, heated in hydrogen and then degassed in vacuum.

To one of these electrodes, a measured volume of standard acridine solution was added "in situ", i.e. without exposure to air. This was made possible by using a slightly modified version of the apparatus shown in Figure XLIX. With the new cell (see Figure XLII, page 244) the electrode was heated under a stream of hydrogen with the stopcock B closed. The electrode was allowed to cool in a stream of hydrogen, and when cooled, the gas outlet tube was sealed off, and the stopcock A closed. Then the electrode was outgassed by opening stopcocks B and C thereby connecting the apparatus to a high vacuum line. When the apparatus was completely evacuated, the vacuum line was disconnected. A calibrated container was opened to the apparatus, and a known volume of "de-oxygenated" acridine solution was allowed to run into the cell containing the electrode, by breaking the glass tip shown in the diagram.

After the usual cleaning operations another electrode was allowed to cool to room temperature in a stream of hydrogen. When cooled, the electrode was transferred to a glass stoppered container attached to the vacuum line for the purpose of removing any residual or loosely adsorbed hydrogen. This meant a brief exposure of the electrode to air for about a few seconds during the transference. After degassing in vacuo the electrode was removed and placed in a glass-stoppered tube containing a known

Figure LII:

Modified apparatus used for comparative study of two
similar electrodes treated by different procedures.

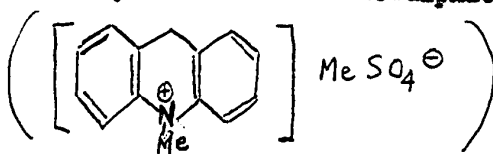


volume of standard acridine solution. This meant that the electrode was again exposed to air for a few more seconds. The total time of exposure was never allowed to exceed 10 seconds. The interesting feature of this experiment was that both electrodes showed equal amounts of acridine adsorption. It would appear therefore that any thin oxide film which might be formed during the brief exposure to air did not affect the adsorbing capacity of the metal markedly. If the electrode was exposed to air for longer periods, then the amount of acridine adsorbed increased considerably. This comparative experiment was repeated several times, and the reproducibility between replicate determinations was found to be about $\pm 2\%$, which was considered satisfactory since the results for several electrodes treated by the first procedure only did not give any reproducibility better than $\pm 1 - 2\%$.

(vii) Preparation and Purification of Reagents Used

Pyridine (Baker Analyzed Reagent Grade) and quinoline ("Refined Grade") were redistilled in nitrogen and in vacuo respectively; acridine (Matheson, Coleman and Bell) was recrystallised from methanol and sublimed.

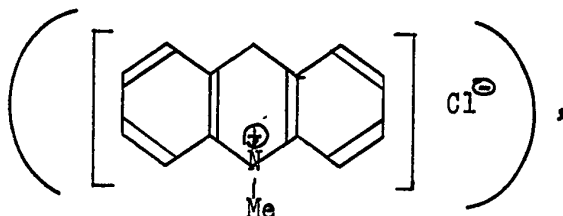
N-methylacridinium methosulphate¹⁹⁷



($\text{C}_{13}\text{H}_9\text{NMe}, \text{MeSO}_4$) was prepared by adding acridine (2 grams) to

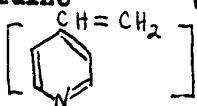
re-distilled nitrobenzene (10 mls) at 160°C , followed by freshly-distilled dimethyl sulphate (2.2 grams). The mixture was allowed to cool at once and poured into ether. After an hour the mixture was filtered giving the methosulphate as yellow crystals in 95% yield. The salt was re-crystallised from methanol and ether.

N-methylacridinium chloride ($\text{C}_{13}\text{H}_9\text{N Me Cl}$),



was prepared from the methosulphate by passing a concentrated aqueous solution of the methosulphate through a strongly basic anion exchange resin (Dowex 1-X8, J.T. Baker Chemical Co.) which had been previously converted to the chloride form. The N-methylacridinium chloride was recrystallised from methanol and ether and the chloride content was checked by volumetric titration with silver nitrate (Volhard's method) and found to be almost quantitatively stoichiometric.

Three isomers of benzacridine, and three isomers of dibenzacridine were gifts from Professor Adrien Albert, Department of Medical Chemistry, Australian National University, Canberra, Australia. These samples were all recrystallised from methanol. Pyrrole (Eastmans) was purified by distillation in vacuo. Indole and carbazole (Eastmans) were recrystallised from water and methanol respectively.

Poly-4-vinyl pyridine¹⁹⁸⁻¹⁹⁹ was prepared from the monomer 4-vinyl-pyridine , which was first distilled under reduced pressure to remove the catechol inhibitor and low molecular weight polymers in the sample. The polymerisation was effected by adding 2 grams of benzoyl peroxide to 100 grams of the monomer (dissolved as a 5% solution in re-distilled oxygen-free toluene). The mixture was allowed to stand in an atmosphere of nitrogen for a few days at 30° C, at the end of which the polymer (a white powder) was filtered off and dried under vacuum.

Poly-4-vinylpyridine butyl bromide, the quaternary salt of the polymer, was prepared by adding an excess of freshly-distilled n-butyl bromide (about 8-10 times the theoretical amount required) to the polymer dissolved as a three percent solution in nitromethane. The mixture was heated under a reflux condenser at a temperature of 65° C for three days. The solution was allowed to stand at room temperature for three more days, and the poly-quaternary salt precipitated out as an amorphous solid. The crude polyelectrolyte was re-precipitated from ethanol and ether. Better yields could be obtained by reprecipitation from ethanol and ethyl acetate.²⁰⁰

Hydrochloric acid and hydrobromic acids used in the experiments were of "Baker Analyzed Reagent" grade.

The methanol²⁰¹⁻²⁰³ used was "acetone free" reagent grade supplied by Brickman and Co., Montreal. It contained

about 1% ethanol, and was further purified by the following procedure. 25 grams of iodine were dissolved in one litre of methanol, and the solution was slowly poured into 500 mls of stirred N-NaOH solution. A small amount of yellow precipitate of iodoform was formed. The solution was kept over-night and filtered. The methanol was refluxed over magnesium with a small amount of iodine for about 5 hours and then fractionally distilled, and a fraction boiling between $64-67^{\circ}$ C was collected. This was again refluxed with a fresh quantity of magnesium in the presence of iodine. This procedure was continued until the distilled methanol gave a vigorous reaction with magnesium. Methanol was finally distilled over magnesium and the fraction boiling at $64-67^{\circ}$ C was collected for use.

Conductance water was prepared by distillation from an alkaline solution of potassium permanganate (made up from "distilled water") followed by another distillation in nitrogen through a column of glass beads at 500° C, and finally a direct distillation in a stream of nitrogen gas purified from carbon dioxide and oxygen, and passed through three traps in liquid air. Where otherwise stated, all adsorption experiments from aqueous solutions were carried out at room temperature using conductance water. The effect of pre-electrolysis²⁰⁴⁻²⁰⁵ of the solution was examined in the case of acridine (vide infra) by electrolysing the redistilled water for 24 hours by

means of a current of 2×10^{-2} amps (at 500 volts) using a mercury cathode 100 cm^2 in area; the water was stirred by means of a stream of purified hydrogen.

C. RESULTS AND DISCUSSION

(i) Adsorption Isotherms

Adsorption isotherms for acridine, quinoline, pyridine, 2,3-benzacridine, 1,2-benzacridine, 3,4-benzacridine, N-methylacridinium methosulphate, N-methylacridinium chloride, 1,2,7,8-dibenzacridine, 1,2,6,7-dibenzacridine, 3,4,6,7-dibenzacridine, pyrrole, indole, carbazole, the polymer poly-4-vinylpyridine and poly-4-vinylpyridine butyl bromide were determined on nickel, copper and silver from aqueous solutions (conductance water $\chi = 5 \times 10^{-7}$ mhos), methanolic, and acidic solutions (HCl , HBr and HClO_4). A selection of the more successful results are shown in Figures LI and LIV. Except where relevant, the discussion will not include reference to many time-consuming but abortive preliminary experiments done during the course of development of the final successful technique.

(ii) Determination of the Solubility of Acridine in Water

In the case of the studies of acridine adsorption, solutions of known concentration in pure water were required.

Figure LIII:

Adsorption isotherms at 25° C for acridine at copper
from solutions made with conductance water, pre-
electrolysed conductance water and distilled water.

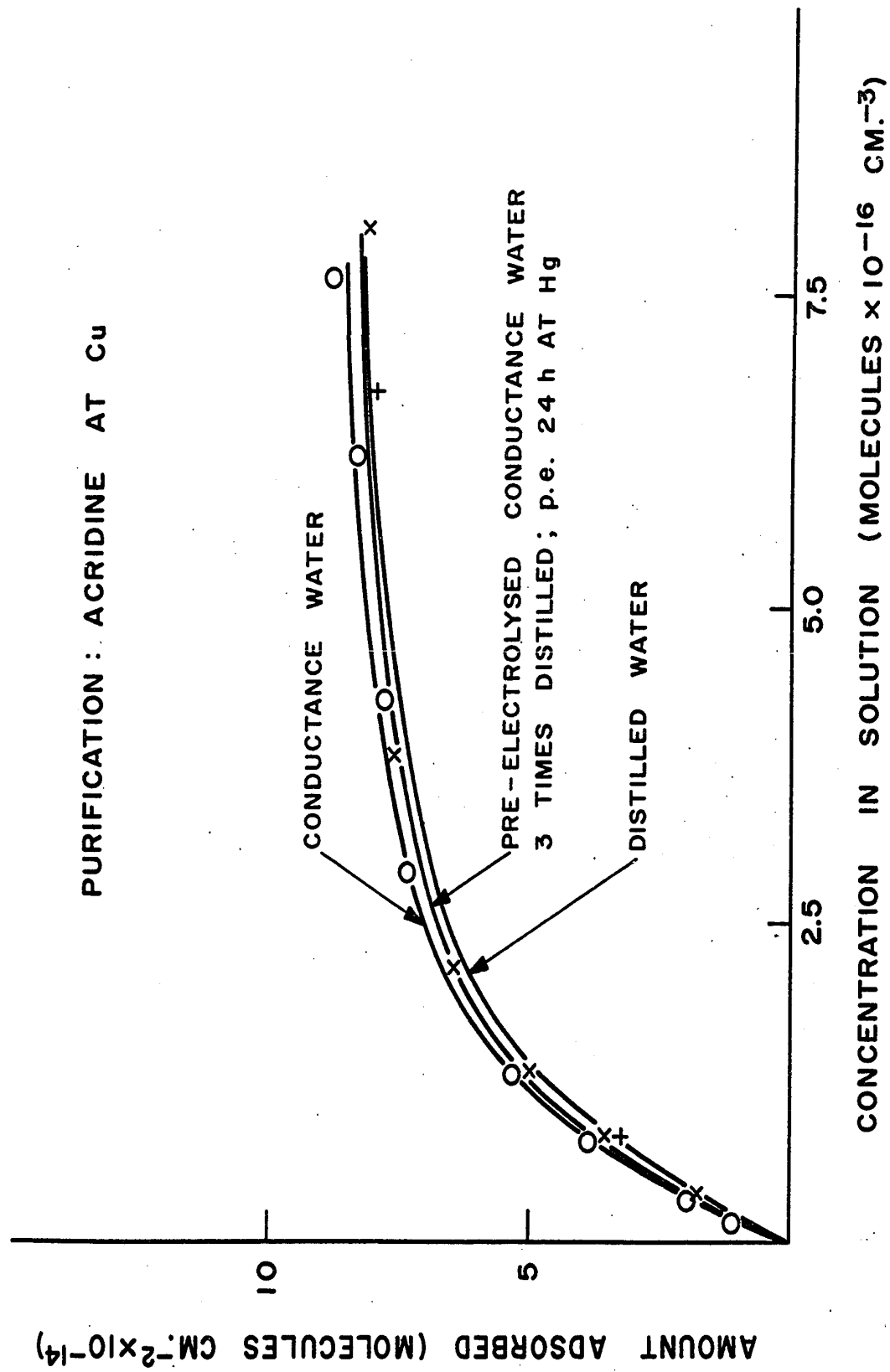
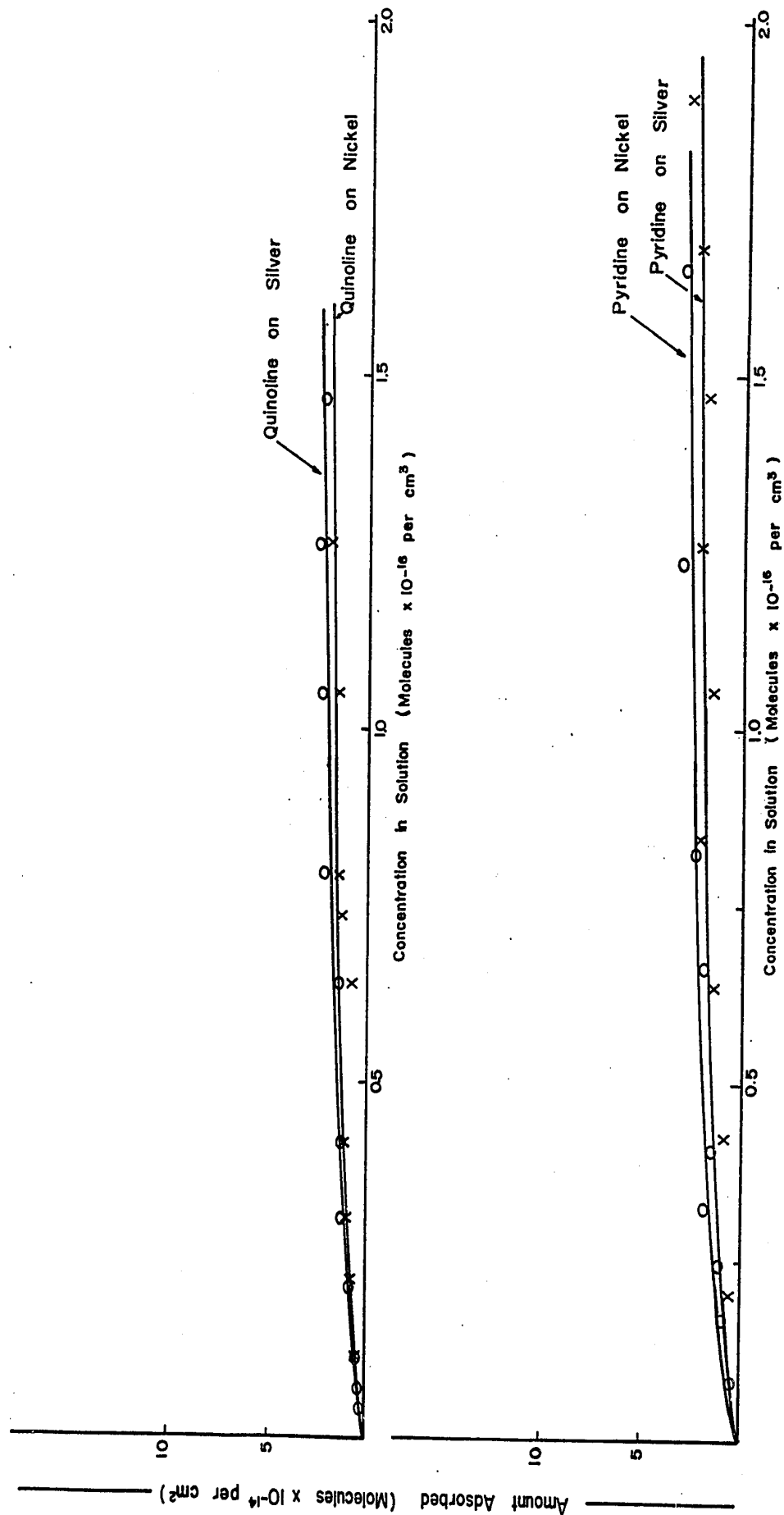


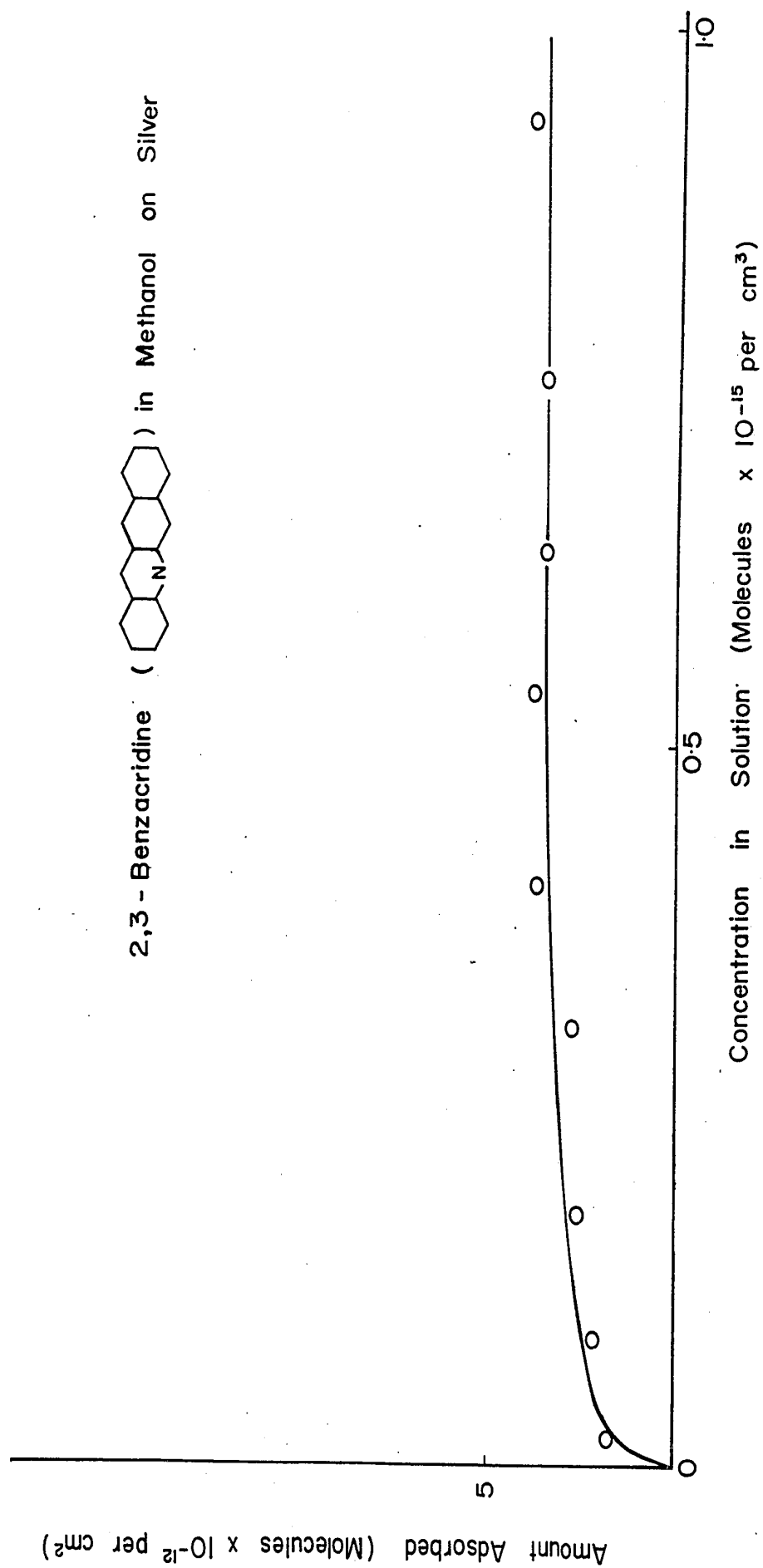
Figure LIV:

- a (i) Adsorption isotherms at 25° C of quinoline on silver and nickel
- a (ii) Adsorption isotherms at 25° C of pyridine on nickel and silver
- (b) Adsorption isotherms at 25° C of 2,3 benz-acridine in methanol on silver
- (c) Adsorption isotherms at 25° C of N-methyl-acridinium methosulphate on copper
- (d) Adsorption isotherms at 25° C of N-methyl-acridinium chloride on copper.

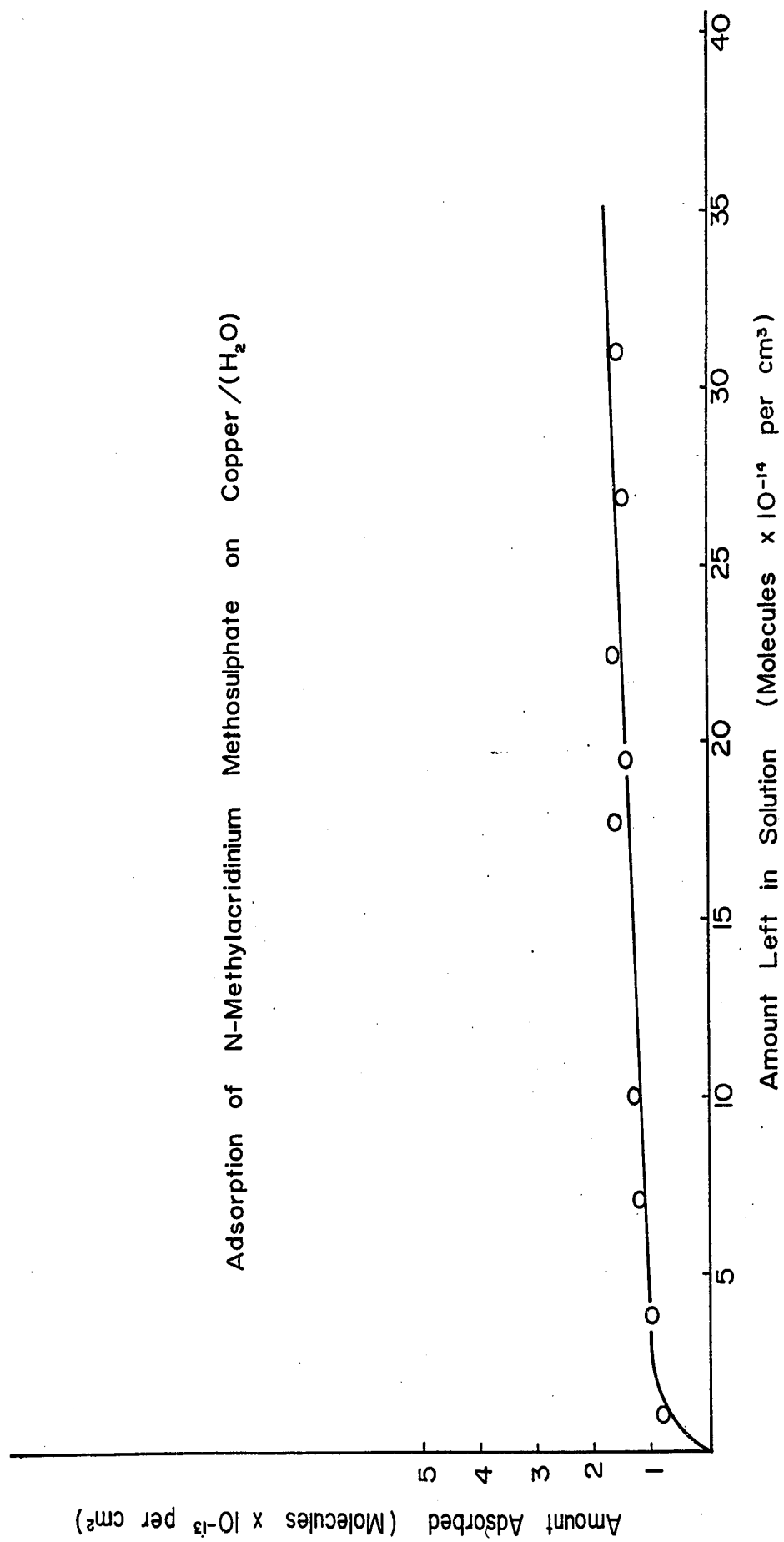
For clarity these figures are shown on the four following sheets.



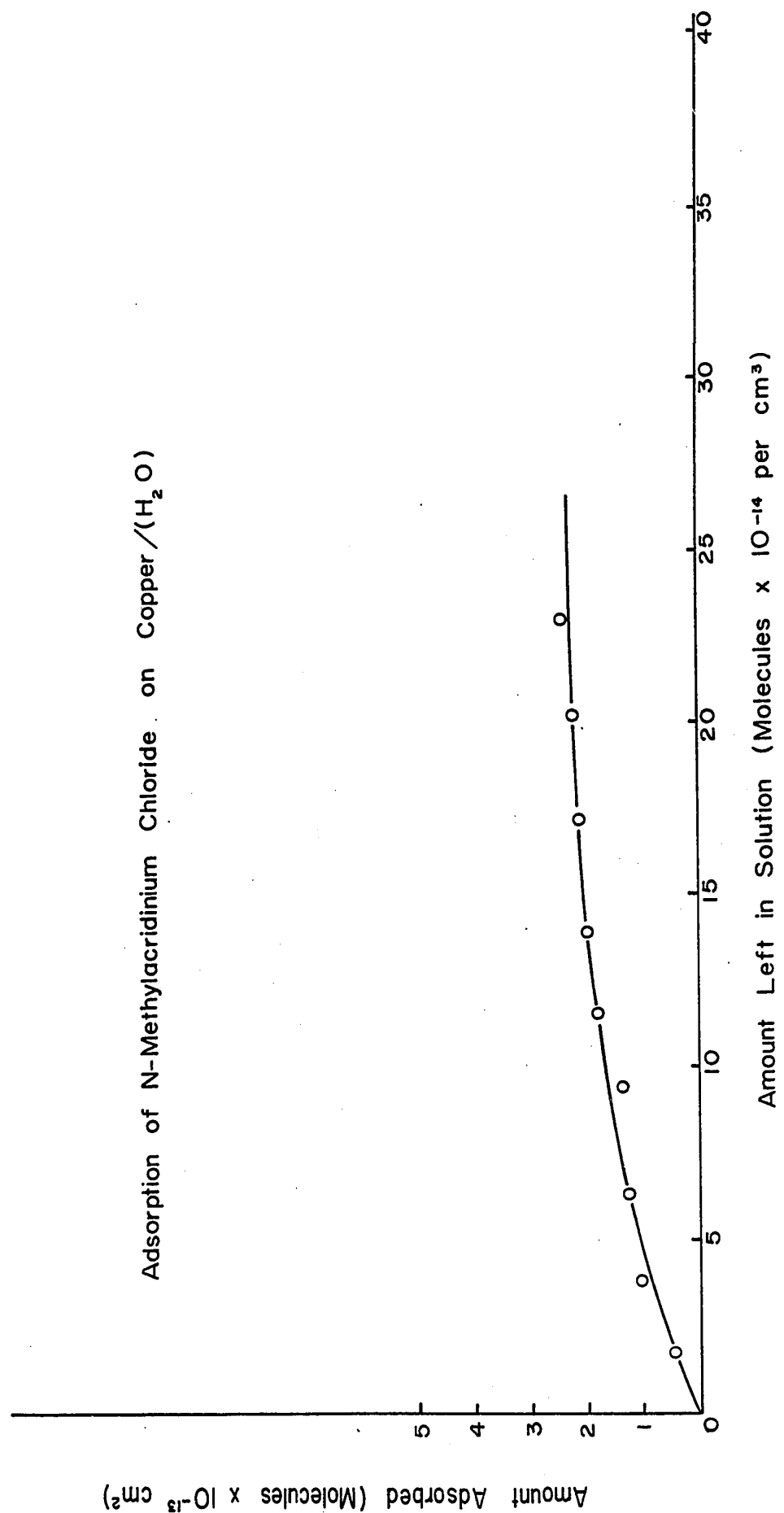
2,3 - Benzacridine (C1CCC2C(C1)C3=CC=CC=C3N2) in Methanol on Silver



Adsorption of N-Methylacridinium Methosulphate on Copper / (H₂O)



Adsorption of N-Methylacridinium Chloride on Copper/(H₂O)



Since this compound is sparingly soluble in water such solutions could not be prepared directly. A saturated solution was therefore first made up in pure water, and its concentration determined spectrophotometrically by conversion to acridinium ions by means of excess aqueous 0.1 N hydrochloric acid, followed by comparison with a standard solution made up from a weighed amount of acridine in 0.1 N HCl (in which the base is of course appreciably soluble). The solubility of a saturated solution of acridine in water was found to be 3.4×10^{-4} M per litre at 25° C. This is a useful method for obtaining quantitative solubility data on organic compounds which are normally listed qualitatively in the literature as "sparingly soluble", "slightly soluble", or "partially soluble". Further solutions of known concentration could then be prepared from the saturated one by dilution.

(iii) Ultra-purification of Water

The effects of ultra-purification of the solution by pre-electrolysis²⁰⁴⁻²⁰⁵ of the conductance water were examined. This purification procedure by pre-electrolysis causes the deposition of trace heavy metals or other depolarisers which may be likely to cause interference. Good agreement within tolerable limits of experimental error was found with solutions made up with (i) distilled water (ii) conductance water and (iii) conductance water pre-electrolysed at a mercury

cathode and a palladium anode at 500 volts for 24 hours. Figure LIII illustrates the results obtained which indicate that ultra-purification is unnecessary for the present adsorption studies at large electrodes. It appears that equilibrium measurements of this kind are less susceptible to impurities than are kinetic measurements on electrode processes. Thus, satisfactory results were also obtained by Devanathan³⁰ and by the present author (loc. cit) in electrocapillary studies without pre-electrolysis. Also, even the smallest additive concentrations used (circa 10^{-6} M) are probably much greater than those of any minute traces of impurities which might remain after the distillation of the solvent.

(iv) Role of Varying Adsorbent

In all the cases examined, copper was found to adsorb the greatest amount of organic additive as compared with nickel and silver for a given solute concentration. This was somewhat surprising because it would be expected from the strong chemisorptive properties of nickel that this metal would adsorb the largest amount of organic additive. For example, copper showed an appreciable adsorption of acridine, at least twice that taken up by nickel from a neutral aqueous solution of the adsorbate at the same concentration. It is clear that competitive adsorption between the acridine and water molecules must occur during the adsorption process. so that this result

may be interpreted as due to stronger chemisorption of water by nickel since the number of positive d-holes in nickel, which enhances adsorption by "electron acceptance" from unshared pairs on O in H_2O or N in NH_3 ,²⁰⁶ is greater than in copper.

Acidic and alkaline solutions of acridine were also examined with nickel, but the presence of nickel ions in solution, which have very strong ultra-violet extinction in the experimental wave-length region, masked the usual absorption peaks due to acridine. Silver adsorbed acridine from aqueous solutions to about the same extent as nickel. For the reasons mentioned above, attention was focussed on the use of copper. Quantitative comparisons of the adsorption behaviour are given below in terms of standard electrochemical free energies of adsorption.

(v) Rôle of Adsorbate Structure

Experiments were performed with copper using pyridine, quinoline, and acridine as adsorbates. Three adsorption isotherms were obtained (see Figure LI), and their heights were in the order of increasing ring size. The equilibrium constant for adsorption was not directly proportional to the number of aromatic rings in the molecules used but the work carried out demonstrates a regularity in the trend of the isotherms. This result is qualitatively comparable with that

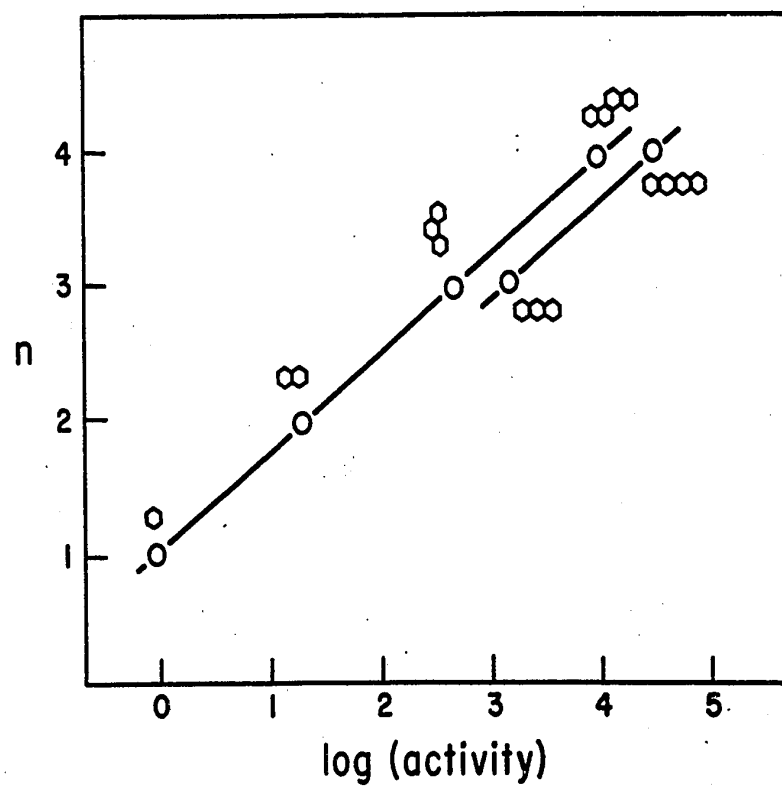
obtained for polycyclic aromatic hydrocarbons adsorbed at mercury,¹⁸²⁻¹⁸⁴ where the degree of adsorption at a given solution concentration has been found to increase with the number of condensed conjugated rings in the molecule (see Figure LV, page 256).

Inspection of Figure LI shows that after the initial inflection in the isotherms, there is still some tendency for the amount adsorbed to increase with increasing solution concentration. This may be due to the heterogeneity of the metal surface or to thermal disorientation of the monolayer which allows some molecules to stand on edge or at an angle to the surface. Cleaned copper, unheated in hydrogen, adsorbs more acridine than the hydrogen-treated metal. This effect is probably due to sintering of surface asperities and also to the fact that any film of copper oxide (because of greater porosity and surface area^a) may be a stronger adsorber than the pure metal surface.

It is observed from the isotherms that the extent and hence the free energy of adsorption of the organic bases at copper at a given solution concentration increases with increasing number of condensed conjugated rings, thus paralleling the trend of heats of sublimation in a homologous series. However, it is not immediately obvious that such a trend should be observed, since each adsorbed organic molecule must cause

Figure LV:

Ring size of aromatic hydrocarbons and their surface activity at mercury (after Frankin, Gerowicz and Rybal'schenko). n = number of rings; $\log(\text{activity})$ is an arbitrary measure of the surface activity corresponding to the concentration of adsorbate required to give a given depression of surface tension by each compound.



the desorption of several water molecules if it lies flat upon the surface, and each water molecule is held to the surface with an heat of adsorption of about 13-18 k.cals/mole.^{207,208} This gain in energy of water molecules is partly made up by interaction of water with π -orbitals of the conjugated rings which may cause a decrease of energy of the water molecules adjacent to the adsorbed organic base of 3-4 k.cals/mole of water.²⁰⁹ The precise nature of the intermolecular bond between the water and the organic compounds is uncertain. It may result from the interaction of the hydrogen atom of the hydroxyl group and the π -electrons of the aromatic system. This idea was proposed by Badger and his co-workers,^{210,211} Finally it is also in agreement with the views of Mulliken²¹² who suggested the possibility of weak hydrogen bonding between the hydrogen atom and the "somewhat negatively charged carbons of the benzene rings".

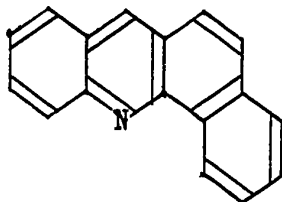
The limiting value of the surface coverage of copper by acridine in the isotherm for copper (heated in hydrogen) corresponds to complete coverage of the metal by a monolayer of acridine molecules lying flat, if we take the area of the acridine molecule as $65 \text{ \AA}^2$, a figure derived from the measurements of a space-filling scale model of the molecule, using a real to apparent area ratio for copper heated in hydrogen as 3.5.²¹³ It follows from the isotherms that at the highest concentration of pyridine and quinoline studied, the surface is not fully

covered by these organic molecules. In these systems, a simple Langmuir isotherm may not be expected to hold for two reasons: firstly, in aqueous solutions, there will be competitive adsorption between the organic molecule and water, and secondly there can be interaction effects between the adsorbed species due to dispersion and coulombic forces (if the additives are present as ions; see below), so that an isotherm of the Temkin type would perhaps be more applicable²¹⁴ under certain conditions (as we show elsewhere in the case of adsorption at mercury).

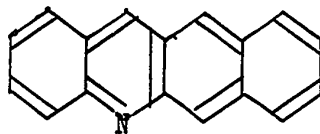
(vi) Further Attempts to Correlate Adsorbate Structure with Degree of Adsorption

Three isomers of benzacridine and three of dibenzacridine were obtained as a gift from Professor A. Albert. The adsorption of these substances was examined at copper, but their solubilities in water were far too low (less than 10^{-6} M) for them to be usefully employed. An analogous series (i.e. of compounds differing from another by one ring) comprising pyrrole, indole and carbazole was explored as a second possibility to study the effect of ring size on adsorption at copper. The solubility of carbazole was again found to be too low for practical use. A further restriction was the absence of any sharp absorption peaks in the ultra-violet spectrum of pyrrole.

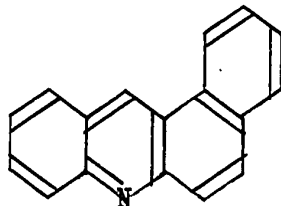
The change of solvent from water to methanol was then made in order to overcome the difficulties presented by the insolubility of the compounds. Methanolic solutions of acridine, pyridine and quinoline were then used with copper, nickel and silver. In all cases Ni and Ag showed very little adsorption of the organic additive. Trace amounts were adsorbed by copper, which confirms the trend already noted that copper is the best adsorbent of the three metals in these experiments. Negligible amounts of 1,2-benzacridine and 3,4-benzacridine were adsorbed on Ni and Ag from methanolic solutions. With copper, only 2,3-benzacridine showed a significant amount adsorbed from a methanolic solutions containing approximately a hundred fold smaller concentration of molecules than that previously used for pyridine, quinoline and acridine (see Figure LIV (b)). This result is not unreasonable if one inspects the structure of the three benzacridines used:



1,2-benzacridine



2,3-benzacridine



3,4-benzacridine

It may be seen that 2,3-benzacridine has the most favourable structure for maximum adsorption in a planar configuration. These results also suggest a parallelism between the degree of adsorption and the solubility* of the adsorbate. Acridine, quinoline and pyridine are very soluble in methanol, while 2,3-benzacridine appears to be the least soluble. An explanation of the negligible adsorption from methanolic solutions is that there exists the usual competition between the interphase** and the bulk phase for the solute, and in the methanolic solution the organic molecule has a lower free energy of solvation than in water. With 2,3-benzacridine adsorption forces "dominate" over the solubility effect, and it is then possible to measure a significant extent of adsorption over a reasonable range of concentrations and obtain an isotherm. The results clearly indicate that the adsorption of 2,3-benzacridine must therefore be very strong; an additional confirmation that the degree of adsorption increases with increasing ring structure.

* This is not the only factor concerned since quite soluble derivatives e.g. quaternary ions of the bases are strongly adsorbed from water at Hg.

** Here we prefer the use of the term "interphase" rather than "interface" as it allows a better description of the 2 phase equilibrium which occurs in adsorption. It also avoids the introduction of fictitious concepts such as adsorption in a 2 dimensional "interface".

(vii) Adsorption of Ionic Substrates

Attempts were made to measure the adsorption of acridinium ions on copper, nickel and silver, Pyridinium and quinolinium ions were not used because of the relatively small amounts adsorbed shown in the experiments with the neutral molecules. To maintain the organic bases in their fully ionised state (i.e. not less than 99.9%), acidified solutions of the substrates must be used; this is to prevent hydrolysis of the ions. However, the presence of excess acidity gives rise to problems of a different and difficult nature, namely the dissolution of the adsorbent. The presence of copper and nickel ions, and/or complexes formed between the metallic ions and the organic compounds tends to mask the ultra-violet absorption bands of the organic adsorbate, thus interfering with the analytical determinations. Copper is insoluble in completely oxygen-free acid solutions, but such ideal conditions can only be achieved experimentally with considerable difficulty. Acidic solutions of acridine, for example, were "de-oxygenated" by continuous bubbling with oxygen-free nitrogen or hydrogen but complete exclusion of oxygen could not be attained. Traces of oxygen can cause sufficient dissolution of copper to interfere with the observation of the ultra-violet spectrum of acridine and other organic substrates.

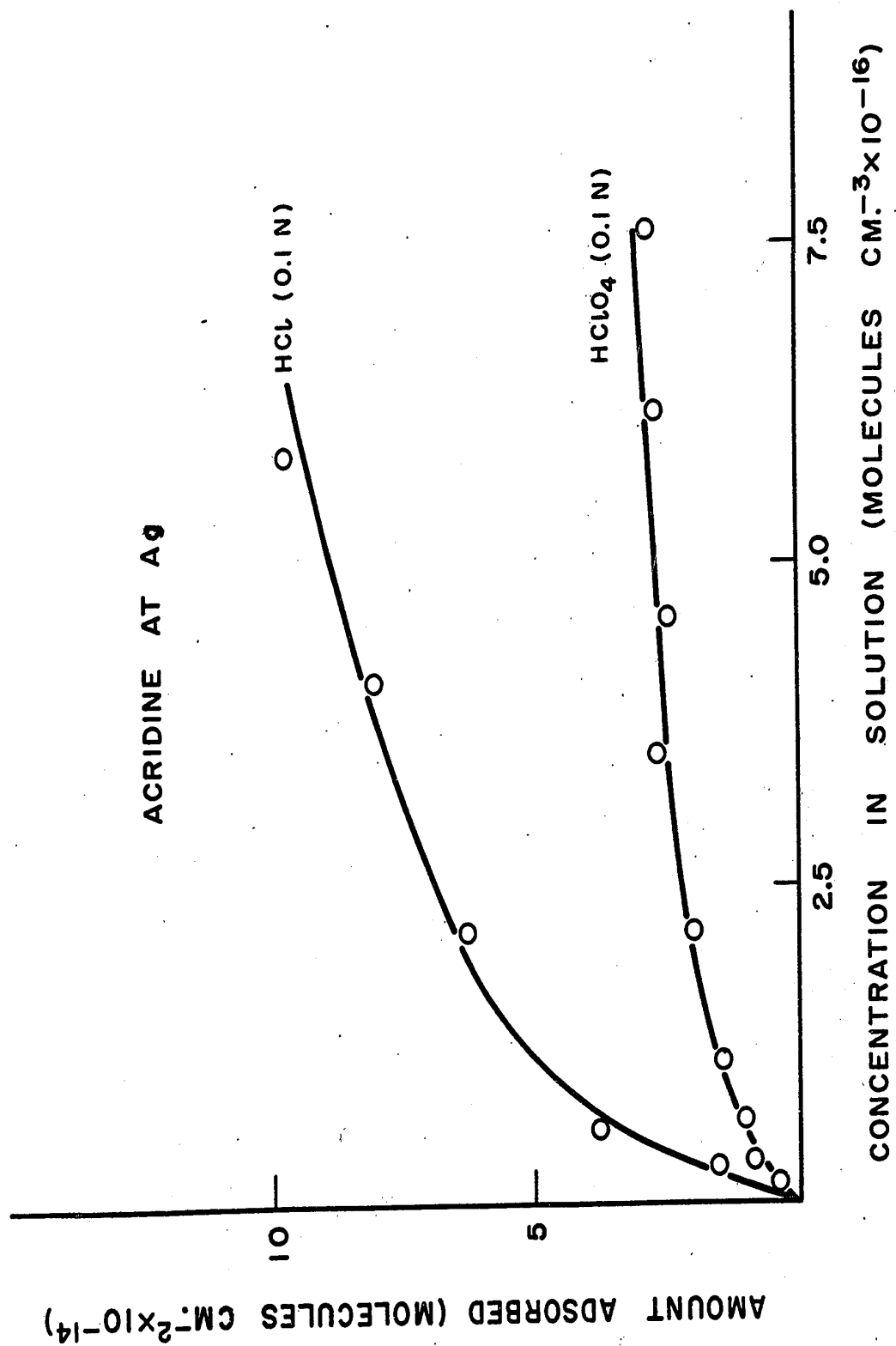
The interference by silver ions, presumably due to

the small solubility of silver chloride, is not serious at moderate concentrations of acridinium chloride, but the extent of adsorption of acridinium ions by the metal was, at all solution concentrations, at least several times greater than the adsorption of the corresponding neutral molecule from a neutral aqueous solution or from a dilute perchloric acid solution. This may possibly be due to adsorption of acridinium ions on the metal surface as well as on the silver chloride, which is well known as a strong adsorbent. The adsorption of the acridinium ion from 0.1 N aqueous hydrochloric and 0.1 N aqueous perchloric acid solutions was examined with the aim of establishing the effect of ionisation of the base upon its adsorption, and the effects of the gegen-anions (Cl^- or ClO_4^-).

Figure LVI, page 263 shows the isotherms at silver at 25°C for the acridinium ion in 0.1 N aqueous HCl and HClO_4 respectively; two interesting facts emerge from these results: (i) the "ammonium type" ion is as strongly adsorbed as the neutral molecule and (ii) the acridinium ion in HCl is more strongly adsorbed than in HClO_4 . It is well known from electrocapillary and double-layer capacity studies at Hg that the Cl^- ion is more specifically adsorbed than ClO_4^- , and the results shown in Figure LVI suggest that in HCl , a synergetic effect is present viz. that the specific adsorption of Cl^- assists the adsorption of the acridinium ion by diminishing the coulombic repulsion between the charge on the adsorbed ions;

Figure LVI:

Adsorption isotherms at 25° C of acridine at silver
from aqueous hydrochloric and aqueous perchloric
acids, respectively.



this effect is less important in HClO_4 where the anion is less specifically adsorbed.

In the acid solutions of the acridine used, the molecule is present in the ionic form to the extent of about 99.99%. Since strong adsorption is observed under these conditions, it is unlikely that the active species in acid solutions of basic heterocyclic corrosion inhibitors is the neutral molecule although it could be in the case of aromatic or aliphatic amines where the N is not in a conjugated ring, as previously suggested.²¹⁵⁻²¹⁷ Strong adsorption of the quaternary ion N-methylacridinium (chloride or methosulphate) was also observed (see Figures LIV (c) and (d)), and for this case there can be no ambiguity concerning the species adsorbed.*

* This possible difference of behaviour may be understood as follows: in the case of heterocyclic bases both the H^+ or N-methyl quaternary ions and the corresponding neutral bases could be adsorbed through the π -orbitals at the N-C bonds so that little difference between their standard free energies of adsorption might be expected (as found in the present work at mercury). However, with aromatic or alicyclic bases no such π -orbital interaction is possible in the quaternary ions whilst in neutral bases, on the other hand, the lone pair orbital on the nitrogen atom is available for interaction with the metal; in fact, in some cyclic amines, the character of the C-N and N-H bonding at the nitrogen centre approaches sp^3 .²¹⁸ The observation²¹⁶ that quaternised aromatic and aliphatic bases are less active as corrosion inhibitors than corresponding solutions of the same bases in acids has led to the suggestion that in the latter solutions it is the neutral molecule which is effective in modifying the kinetics of the partial reactions proceeding in the electrochemical corrosion of iron.

Further evidence concerning the identity of species adsorbed from solutions of heterocyclic bases is afforded by the following considerations. We have previously shown (Table VIII, p. 170) that the free energies of adsorption of the bases in neutral and ionic form were surprisingly similar. This might have arisen if the neutral molecules (or the ions) were adsorbed in both the neutral and the acidic solutions despite the fact that in the latter case the concentration of neutral molecules would be very small. From our results (p. 200 et seq.) on the adsorption of pyridine in HCl and N-methyl-pyridinium chloride (MePyCl) in HCl, it is possible to make a direct comparison between the electrochemical free energies of adsorption $\Delta \bar{G}_{ads}^{\circ}$ of pyridine and MePyCl and the data are shown below

Comparison of Electrochemical Free Energies of Adsorption ($\Delta \bar{G}^{\circ}$)

Adsorbate	at $E_{cal} = -800$ mV	at $E_{cal} = -1000$ mV	
	$\theta = 0.25$	$\theta = 0.25$	$\theta = 0.5$
Pyridine ^o	- 4.2	- 4.8	- 4.8
Pyridinium ⁺	- 4.7	- 4.7	- 3.5
MePy ⁺	- 4.2	- 4.9	- 4.7

It is seen that at given potentials the values of $\Delta \bar{G}_{ads}^{\circ}$ for pyridine are in close agreement with those for MePyCl for which there is no ambiguity concerning the identity of species adsorbed. This comparison is regarded as legitimate since the quaternary ion differs from the protonated ion only by one CH₂ group. It is therefore concluded that the species adsorbed from pyridine solutions in aqueous HCl are predominantly the pyridinium ions and that the comparison between the electrochemical free energies of adsorption of neutral and protonated ions (Table VIII) is meaningful and legitimate.

(viii) Effect of Applied Potentials

The effect of applied potentials could not be satisfactorily followed with copper and nickel electrodes because of the problems already stated (*vide supra*). The presence of nickel and copper ions masks the u.v. spectra of the organic molecules. However, Zadwidzki¹⁹⁶ was able to show with quinolinium chloride in 0.1 N aqueous HCl at Ag electrodes, that adsorption can be followed as a function of electrode potential since reduction did not occur until the potential of the electrode was more negative than -0.45 volt with respect to a 0.1 N aqueous HCl-calomel electrode in the same solution. With acridinium chloride, electrochemical reduction occurred with facility when the electrode was polarised cathodically with respect to an hydrogen electrode in the same solution. In this case, the reduction interfered with the determination of the acridine. Nevertheless it is of interest to note that the method can provide a useful way of following the electrochemical reduction of acridine and other substrates (as we have mentioned above) since the rate of loss of acridine and the rate of formation of its principal reduction product, acridan, can be determined simultaneously in very dilute solutions (down to 10^{-6} M). (See Figure LVII).

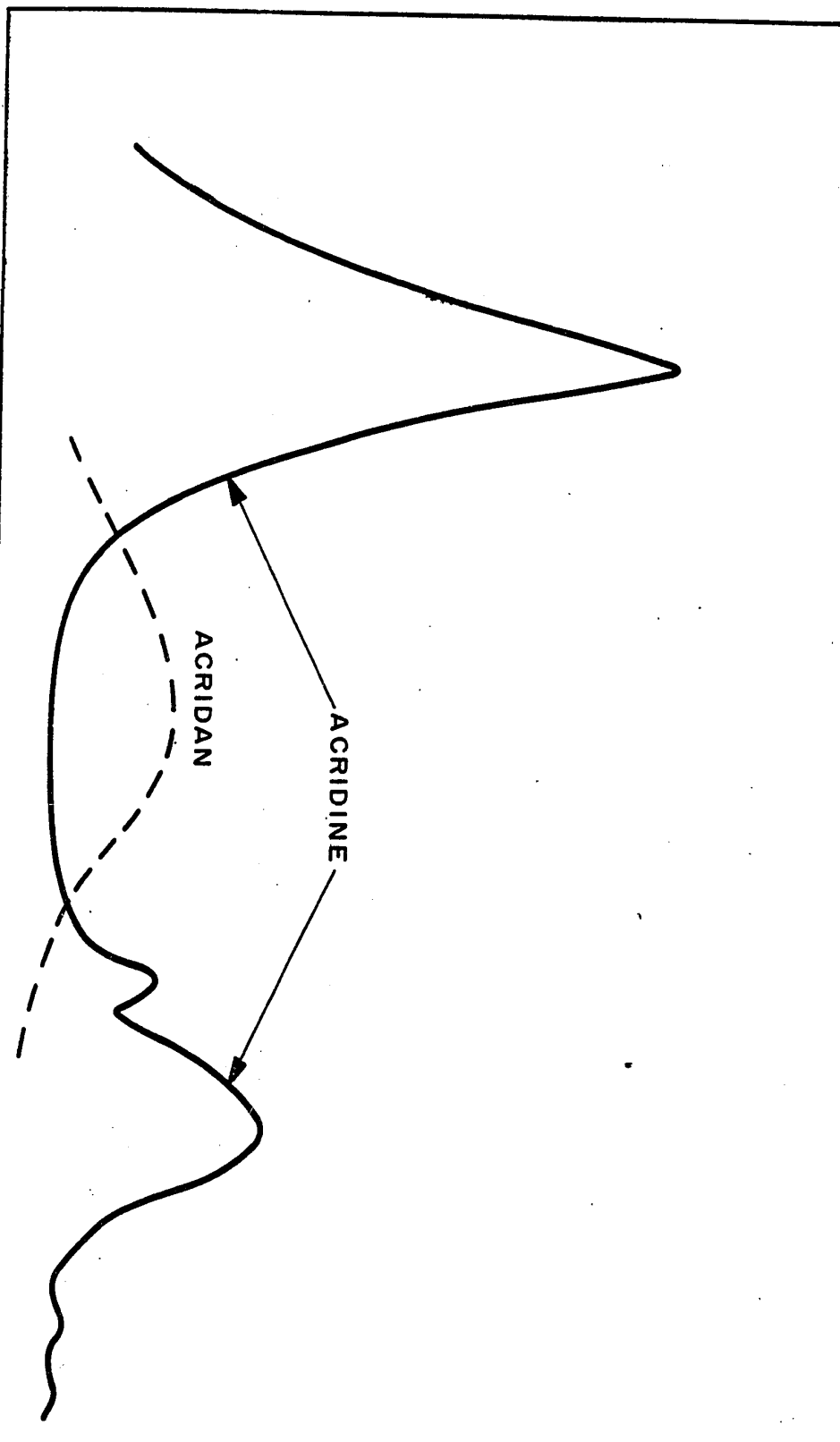
Despite the apparent lack of success in following the adsorption behaviour over a range of applied potentials

Figure LVII:

Ultra violet absorbance spectra for acridine (bold line) and acridan (dotted line). For acridine the three adsorption peaks occur at $260\text{ m}\mu$, $340\text{ m}\mu$ and $354\text{ m}\mu$. The absorption maximum for acridan occurs at $290\text{ m}\mu$.

ABSORBANCE →

WAVE LENGTH →



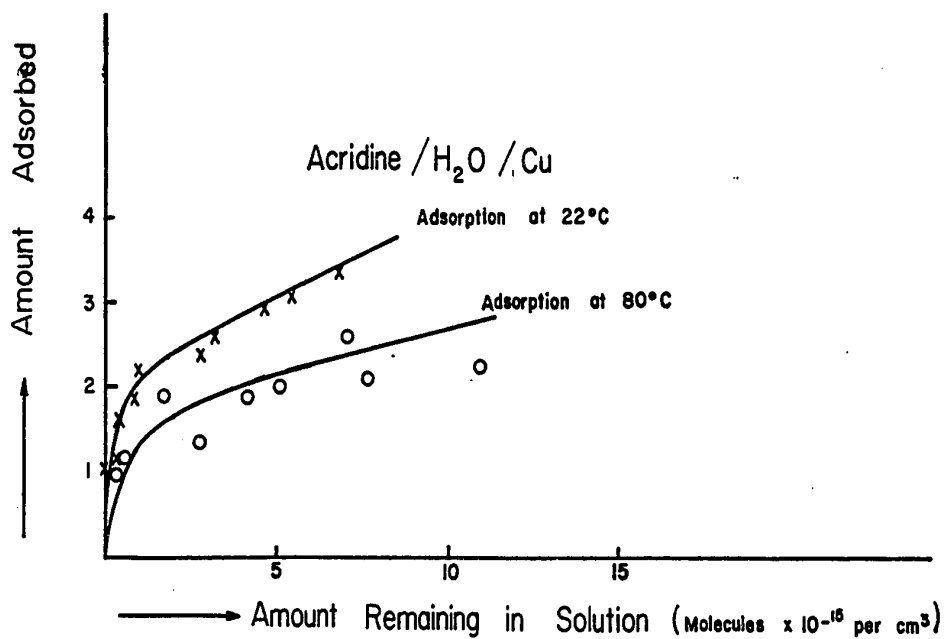
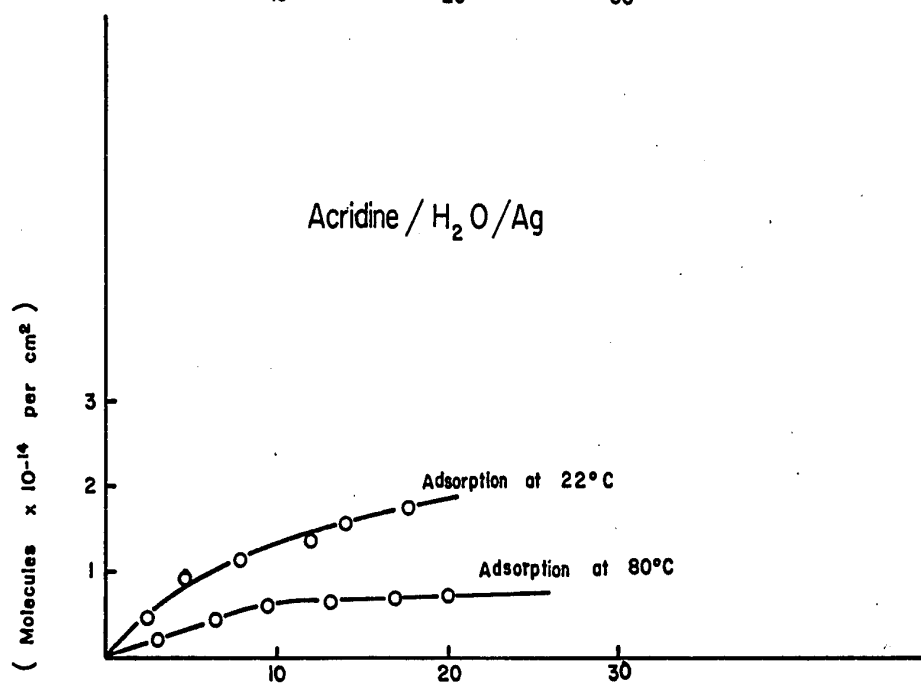
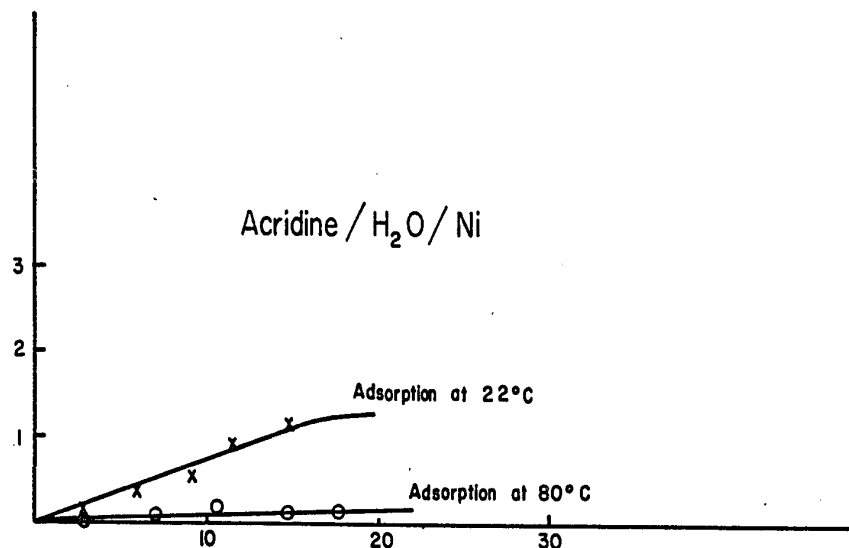
with electrodes of copper, nickel and silver, it may be expected that such studies could be made successfully with electrodes of more noble metals, such as platinum, gold, or iridium. The experiments were not pursued because of the prohibitive cost (\$1500 was quoted!) of obtaining large gauze electrodes of sufficiently fine mesh from these precious metals.

(ix) Standard Electrochemical Free Energies of Adsorption and the Form of the Isotherm

In order to investigate the form of the isotherm which could represent the results (see Figure LVII) and to compare the behaviour of the adsorbates at the solid metals with that at Hg, the standard electrochemical free energies of adsorption $\Delta \bar{G}^0$ have been calculated according to equation (118) and are plotted as a function of surface coverage θ . The values of θ were obtained from Γ_A values from Figure LI, page 241 as in the case of adsorption at mercury discussed in the earlier section of the thesis. The following $\Gamma_A^{\max}$ values were estimated from using the following planar projected surface areas: derived from scale atomic models: acridine $65 \text{ \AA}^2$, quinoline $53 \text{ \AA}^2$, and pyridine $38 \text{ \AA}^2$. The real to apparent area of copper was taken as $\frac{213}{3.5}$ and that of nickel was assumed to be the same. Accordingly,

Figure LVIII:

Adsorption isotherms at 22° C and 80° C for acridine
on nickel, silver and copper.

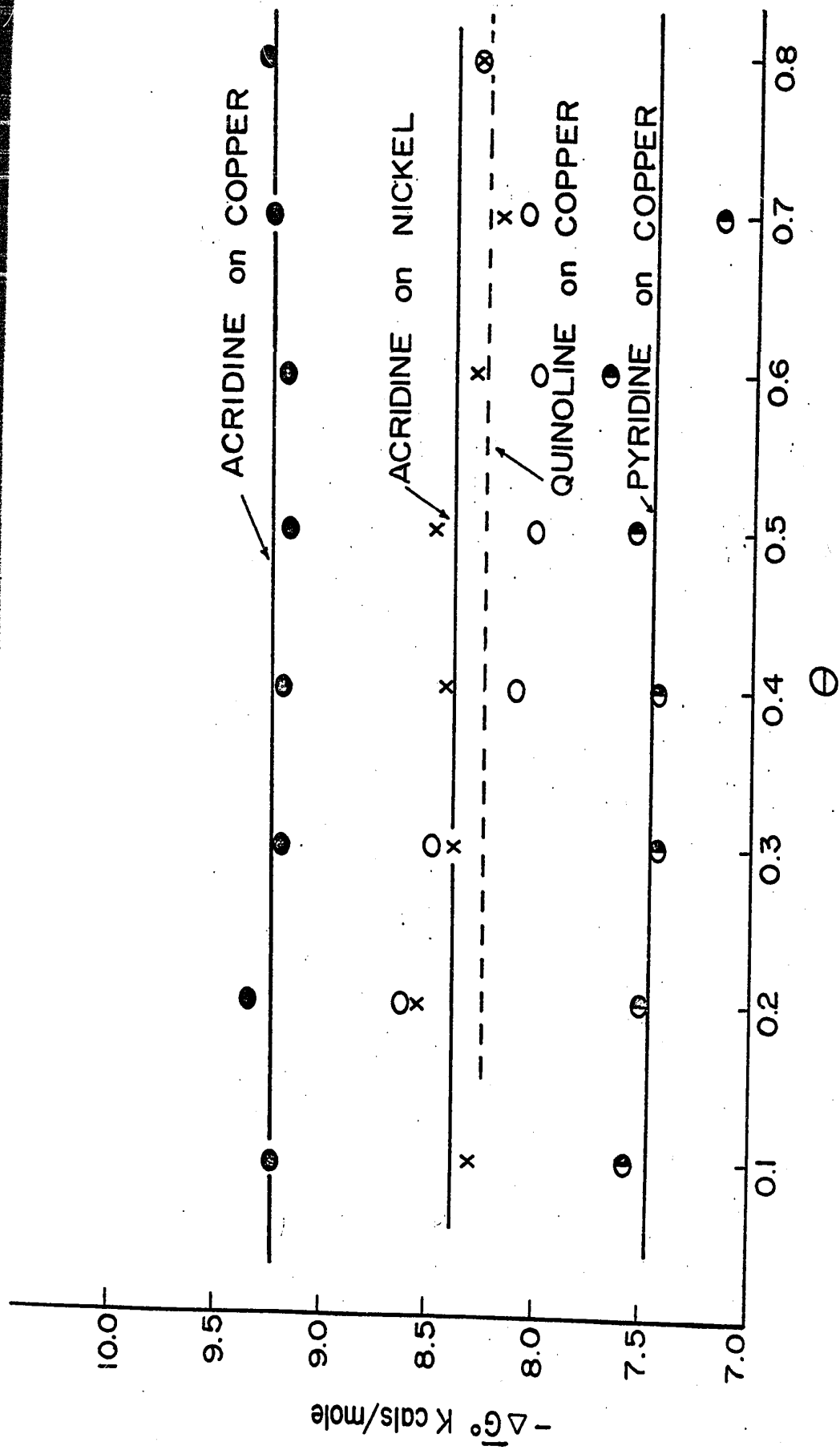


the maximum coverages by the heterocyclic bases were estimated to be 5.4×10^{14} , 6.7×10^{14} , and 9.1×10^{14} molecules/cm² for acridine, quinoline and pyridine respectively. In contrast to the case of adsorption at mercury (at high coverage), it would appear from Figure LIX that the molecules tend to lie flat on the metal surface. The plot for quinoline (dotted line) departs somewhat from linearity especially at low coverage (below 30%). This may possibly be due to the experimental uncertainty in the determination of the isotherm at low coverage. The best experimental results have always been obtained with acridine, and Figure LIX demonstrates quite clearly that $\Delta \bar{G}^0$ is independent of θ for this adsorbate on nickel and copper as distinct from the case of polarised mercury surfaces where there is evidence of sharp changes in slope in the plots of θ (or $\theta^{3/2}$) versus $\Delta \bar{G}^0$ for several adsorbates. It is tempting to attribute this difference to the greater tendency for π -orbital interaction with the transition and neighboring metals, Cu and Ag, than at Hg which has less "transition metal character" than Cu or Ag.

The independence of $\Delta \bar{G}^0$ upon θ shown in Figure LIX indicates that over a surprising range of surface coverage the Langmuir isotherm is applicable. Under conditions where there is little orientation, i.e. for low fields, low degrees of coverage and least π -deficiency (e.g. in aniline and 2-amino-pyridine) in the adsorbate, this is also the case for Hg;

Figure LIX:

Variation of electrochemical free energy of adsorption $\Delta \bar{G}^0$ against the surface coverage θ for acridine on copper and nickel, quinoline on copper and pyridine on copper.



however, at higher fields or surface coverage, orientation appears to occur more readily at mercury than at the solid metals, and $\Delta \bar{G}^o$ is then a function of θ and an isotherm of the Temkin form is then applicable. The tendency for the molecule to be adsorbed in the "flat configuration" will presumably be determined, amongst other factors, by the π -orbital interaction which is then possible with the metal; such orientation will then give minimal dipole interaction since in two dimensions the flat heterocyclic bases will be oriented at random.

It is still puzzling why under these conditions $\Delta \bar{G}^o$ does not increase with θ on account of van der Waals interactions. A possible explanation may be that as the surface concentration of organic molecule increases and that of water decreases, the energy of displacement of the latter will tend to increase and compensate coincidentally the higher energy of adsorption of the organic adsorbate with increasing coverage.

(x) Heats and Entropies of Adsorption

The spectrophotometric method was also applied to the determination of isosteric heats of adsorption ΔH^o of acridine at copper by obtaining the isotherms at different temperatures, and applying the integrated form of the Clausius-

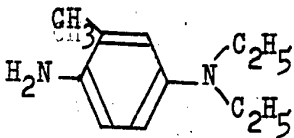
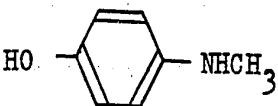
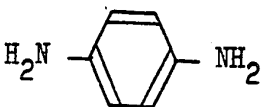
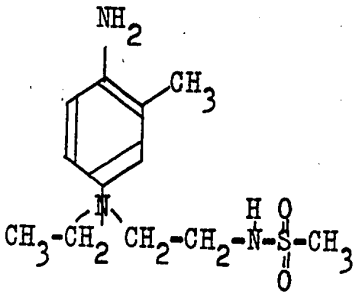
Clapeyron equation;²¹⁹ at half-coverage of the metal surface, the heat of adsorption may be calculated as about 5 kcal/mole. However for the adsorption of acridine at silver or nickel the isosteric heat of adsorption at half-coverage could not be calculated (see Figure LVIII) since over the range of concentrations studied, comparable surface coverages were not obtained at the two temperatures examined and even at lower coverages the same problem remains (see p. 267). Values of ΔH° were also estimated for acridine on copper and silver at lower surface coverage and the results are tabulated below together with the corresponding ΔS° values derived from ΔH° and ΔG° values.

TABLE XII

Function	Coverage θ				Probable error
	0.2	0.3	0.4	0.5	
ΔH° (Cu) kcal. mole ⁻¹	- 5.8	- 5.1	- 5.4	- 4.9	± 0.5
ΔS° (Cu) e.u.	11	14	13	14	± 2
ΔH° (Ag) kcal. mole ⁻¹	- 3.8	- 3.9	- 4.1	-	± 0.5
ΔS° (Ag) e.u.	14	14	14	-	± 2

In view of the usual experimental difficulties involved in estimations of isosteric heats of adsorption, the values shown above are probably only significant to the first figure. These values do not compare too unfavourably with the ones given by Newmiller and Pontius²²⁰ for the adsorption of organic photographic developers on silver, using a technique based on the published method reported in this thesis. Their results are summarised below:

TABLE XIII

Substance	Structural Formula	$-\Delta H^{\circ}$ in kcal mole.
4-amino-3-methyl-N,N-diethylaniline		11 - 12
p-methylaminophenol		approx. 3
p-phenylenediamine		5 - 6
4-amino-3-methyl-N-ethyl-N-(β-methylsulphonamide ethyl)-aniline		12 - 13

The values of $-\Delta H^{\circ}$ given above are an average of a number of values from 50% to 80% surface coverage.

The significance of the heat of adsorption value for acridine at copper is complicated by (1) the fact that upon adsorption of the acridine molecule several water molecules must be desorbed from the surface so that the figure obtained for $\theta = 50\%$ represents a relative heat of adsorption, and is not simply the heat of interaction of the molecule with the (partially covered) surface, and by (2) the fact that the isotherms at low temperature do not reach the same "saturation value" as at higher temperatures. This, however, is a problem which is not confined to the present case, and similar behaviour has often been observed²²¹ in the study of adsorption over a range of temperatures. If allowance is made for the heat of adsorption of several water molecules corresponding to the area occupied by the adsorbate molecule lying flat upon the surface, and for the fact that these water molecules are returned to the bulk phase with an energy change approximately equal to the difference between the heat of adsorption from the gas phase²⁰⁸ and half the heat of vaporisation of water, one obtains a heat of interaction, e.g. of acridine with the copper surface of the order of 30-35 kcal/mole. This would be high for a physical adsorption process but the relatively large value deduced is probably due to other effects including, for example, the π -orbital interaction of the conjugated rings with the surface as demonstrated by Gerowicz¹⁸² in the case of adsorption of naphthalene and anthracene at Hg and also in the

case of heterocyclic bases (pyridine etc.) at mercury examined in the present work. Such a high heat of adsorption may well be a case of "weak chemisorption" as pointed by Wolkenstein²²³ or involve opening of the conjugated rings as discussed in the Appendix, for other aromatic or conjugated heterocyclic molecules.

From the $\Delta \bar{G}^0$ values discussed above and the experimentally determined isosteric heats of adsorption, it is possible to estimate the standard entropies of adsorption which are recorded in Table XII. The main point of interest in these ΔS^0 values is that they are positive, while in the case of adsorption from the gas phase, entropy changes are usually negative on account of loss of degrees of freedom of the adsorbate upon adsorption at the interface. An explanation of this apparent anomaly follows, however, from the statement made above, namely that upon specific adsorption of the organic solute, displacement of several water molecules from the surface must occur, the adsorption of the organic additive being competitive with that of water as discussed previously (Chapter IV, A, iv). This release of water molecules will be accompanied, per mole, by a positive entropy change of the order of the entropy of fusion of water. Since the organic molecule will be equivalent in area to about eight water molecules it may be understood how a net positive entropy change can result.

(xi) Summary

A novel method has been developed for the direct determination of the adsorption of conjugated organic molecules or their ions at solid metals under equilibrium conditions. The requirement of conjugation arises, since, in this method, the determinations of the concentration of the adsorbate in solution are based on the direct measurement of the absorbance of the solution at a suitable wave length in the ultra-violet or visible absorption spectrum of the compound.

Although, during the course of the work, it became apparent that the method suffers some limitations on account of (i) the necessity of using conjugated solutes and (ii) the possibility of electrocatalytic reduction of the adsorbate under cathodic polarisation, it has nevertheless enabled direct comparisons to be made between the behaviour of solid metals and mercury with respect to adsorption of electrochemically interesting solutes such as heterocyclic bases and their ions. In this respect the development of the method must be regarded as successful* since the adsorption can be determined

* Since publication of the present method and results obtained therefrom¹⁸⁷⁻¹⁸⁸, Pontius and Newmiller²²⁰ have adopted the same technique in their studies of adsorption of photographic development on silver and have been able to clarify the rôle of adsorption in the mechanism of photographic development.

at true equilibrium whereas with other methods, e.g. use of radio-tracers and determinations of electrode capacity, this thermodynamic requirement cannot always be realised in practice¹⁹³ and, as a consequence, very little thermodynamically unambiguous data have hitherto been obtained for adsorption of organic solutes at solid metals. It is clear that the method can be further developed e.g. by use of fine electrode gauzes of a noble metal over a range of "anodic" potentials where no hydrogen can be generated and no attack of the metal can occur. Owing to the difficult technical problems already encountered in the work reported and to the unavailability of such an electrode material at the time of development of the method, this aspect of the work could not be pursued further by the present author.

APPENDIX

A. GENERAL OUTLINE

In the introduction of this thesis a comprehensive review on electrochemical matters of direct relevance to studies of electrochemical adsorption was presented. Much (e.g. 84, 57, 63), though not all (e.g. 31, 182, 183) of the previous work in the field of adsorption of additives at electrified interfaces has been concerned either with the effects of these compounds on the kinetics of electrochemical reactions or with their effects on the nature of the double layer. The complementary problem of the nature of the specific adsorption forces involved in the additive-metal interaction at electrodes has received less consideration although some of the "chemical" factors have been discussed (216) in relation to adsorption at iron. A number of other factors have, however, been examined in some detail in regard to gas-solid heterogeneous reactions and to the corresponding adsorption equilibria involved in such reactions. It is the purpose of this Appendix to bring together some of the more important factors determining adsorption forces at metals and to examine more particularly those aspects of the subject which have some interest and relevance to electrochemical adsorption of additives as studied

in the present work. A full review of the subject of adsorption at metals will hence be regarded as being outside the scope of this thesis, and adequate and comprehensive reviews have appeared elsewhere.

B. NATURE OF ADSORPTION FORCES AT THE METALLIC SURFACE

(1) Van der Waals Forces^{179,222}

These are the attractive forces which lead to physical adsorption and arise in the adsorption of non-polar as well as of polar molecules. They are mainly the London "dispersion" forces, a term describing²²⁴ the close connection between their origin and that of optical dispersion. The interaction energy between a pair of atoms may be represented as

$$E_w = \frac{A_1}{r^6} - \frac{A_2}{r^8} + \frac{R}{r^n} \quad (144)$$

where A_1 , A_2 and R are constants dependent upon the nature of the atoms. In equation (144) the first term is due to interactions between mutually induced dipoles and the second term is due to interaction between mutually induced dipoles and quadrupoles and the third term is one of repulsion. In the repulsion term, n is usually taken to be 10-12.

Frequently, in numerical calculations of adsorption energies, only the first (attraction) term is used, because it

is usually assumed that the repulsion term and the second attraction term are approximately equal and opposite. London derived the following approximation for A_1

$$A_1 = \frac{3 \alpha_1 \alpha_2}{2} \left(\frac{h \nu_1 \nu_2}{\nu_1 + \nu_2} \right) \quad (145)$$

where α_1 and α_2 are the polarisabilities of the interacting atoms, h is Planck's constant, and ν_1 and ν_2 are the characteristic frequencies of the optical dispersion curve of the atoms. Slater and Kirkwood²²⁵ derived another approximation for A_1 and this form of the interaction term has been used in the interpretation of adsorption data obtained in the present work (see Chapter III, A (v)). The treatment given above may be extended from the interaction between two isolated molecules to the situation of the mutual interaction of molecules with metals.

(11) Interactions of Non-polar Molecules with Metallic Surfaces

When non-polar molecules approach a conducting surface, the Van der Waal's forces must be modified to include increased repulsion. Margenan and Pollard²²⁶ have shown that a metal cannot be treated as "ideally polarisable", i.e. the fields of the continually changing dipoles in a non-polar

molecule fluctuate so rapidly that induction of polarisation amongst the conduction electrons in the metal cannot follow their fluctuations. In Margenan and Pollard's treatment the metal is regarded as behaving as a dielectric body giving two interaction terms: one from polarisation of the adsorbed molecule and the other from the polarisation of the metal. The second term leads to a positive energy contribution representing repulsion but nevertheless, the total energy of interaction is inversely proportional to the third power of the shortest distance between the adsorbate molecule and the surface (r_0). The most serious drawback in calculating adsorption energies is the lack of an exact knowledge of the distance r_0 , which is determined by the equilibrium of all attraction and repulsion forces acting on the adsorbate atom or molecule. Related lattice and sublimation energies on the other hand can be accurately calculated because the distance between ions and molecules are well known from X-ray diffraction data.

(iii) Physical Adsorption of Ions and Polar Molecules on Metal Surfaces

Both polar molecules and ions interact with metals in a way that is best described in terms of image forces, i.e. an electric charge of opposite sign which may be

mathematically considered to form below the surface at a distance equal to that between the actual inducing charge and the surface. The image force for an ion is given by

$$F_1 = \frac{z^2 e^2}{4 r^2} \quad (146)$$

where z is the number of elementary charges on the ion, e the charge on the electron and r is the distance between the ion and the surface; the contribution to the adsorption energy is then¹⁷⁴

$$E_1 = - \frac{z^2 e^2}{4 r_0} \quad (147)$$

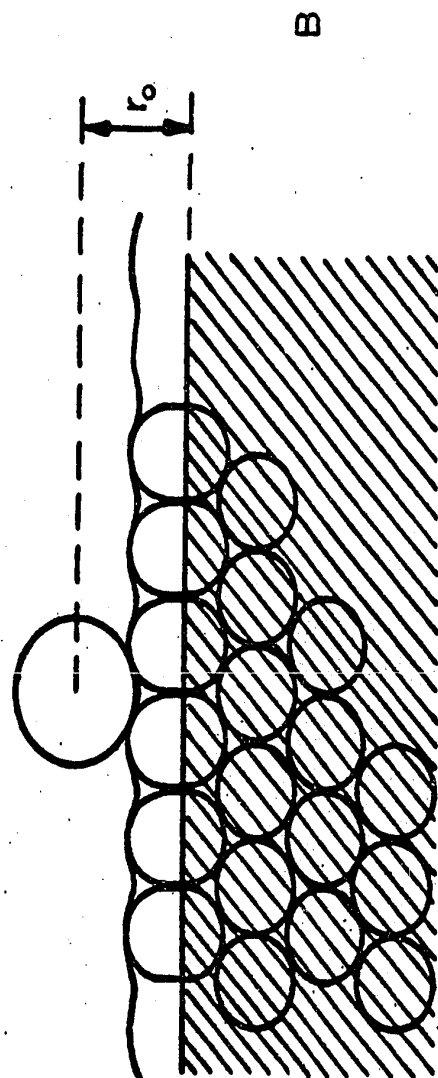
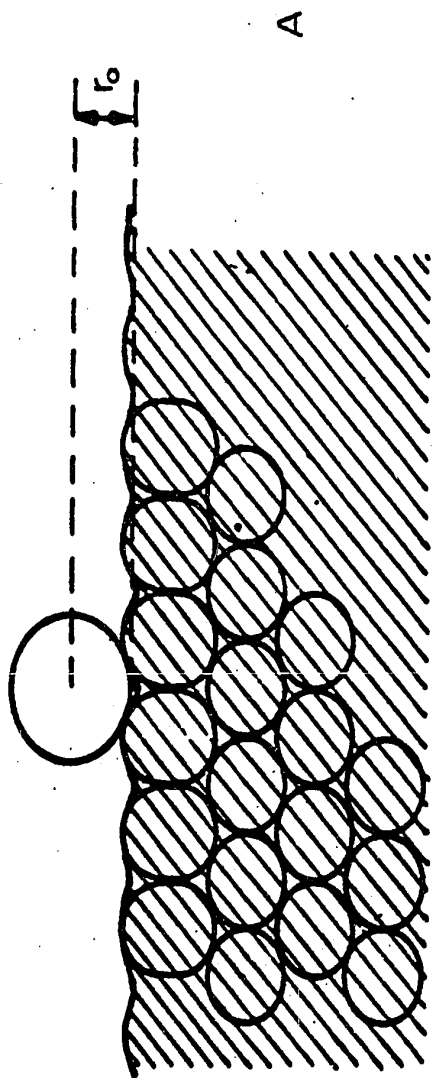
where r_0 is now the equilibrium distance* between the ion and the metal surface.

The problem of assigning a meaningful value for r_0 can be seen from the following considerations. Frequently this distance has been assumed to be the sum of the "radii" of the adsorbed atom and a surface atom. These radii are then derived from experimentally determined figures of distances of the same atoms in other combinations. In some instances calculations have been made with the "Van der Waals radii" (see Figure LX page 283). Inspection of Figure LX²²⁷ will show that the nature of

* It should be noted that the applicability of this image potential equation to the ion-metal interaction at distances r_0 , comparable with atomic radii, has been questioned.³¹⁰ The "discontinuous" nature of the metal surface, as seen by the adsorbed ion, will render the basis of the image potential relation incorrect at short distances.

Figure LX:

Dependence of the adsorption force on the polarisability of the adsorbent: the interaction distance r_0 , between the adsorbed molecule and surface is far smaller if the region of "ideal polarisability" starts at the outer peripheries of the atoms of the adsorbent (Van der Waals radii, see A) than if this region starts at a plane through the centres of outer atoms (see B).



metal surfaces presents a second serious difficulty in the calculation of r_0 and hence the adsorption energies. When the adsorption forces depend on the polarisability of the adsorbent, the effective distance between the adsorbed molecule and the surface is far smaller if the region of "ideal polarisability" begins at the outer peripheries of the atoms of the adsorbent than if this region starts at a plane through the centres of the outer layer of atoms. In the case of "ideal polarisability", better fit with experiment seems to be obtained when the boundary is drawn through the centres of surface atoms; however, when electron transfer occurs in adsorption, the effective boundary appears to be the periphery,²²⁸ although this case, of course, is strictly one of "chemisorption".

The interaction of a dipolar molecule with a conducting surface can also be expressed in terms of image forces and the corresponding energy is given by

$$E_{\mu} = -\mu^2/16 r_0^3 (1 + \cos^2 \theta) \quad (148)$$

where μ is the dipole moment and θ is the angle between the direction of the dipole and the normal to the surface.

E_{μ} is low and in most cases may be neglected.

(iv) The Induced Surface Dipole

A more important interaction between a non-polar atom

or molecule and a conducting surface is provided by the dipole induced in the adsorbate. Two types of experimental evidence have been given for this effect: (a) the two dimensional Van der Waals equation can often be applied to the behaviour of adsorbates such as A , N_2 , O_2 , CO and CH_4 on graphitic materials or charcoal, or on mercury.²²⁹ The striking feature is that the attraction constant required to fit the experimental data is either very low or negative. Repulsion between similarly directed induced dipoles would explain this finding. This behaviour points to a polarisation of the adsorbed molecules by the field of the charcoal or of mercury; (b) values of contact potentials measured by Mignolet^{230,231} showed a large change when xenon was adsorbed on nickel. The "NiXe" film was found to exhibit a surface potential of + 0.85 volt. A number of other physically adsorbed films have also been examined by Mignolet.^{232,233,234} In the case of NiXe, Mignolet showed that each Xe atom had an induced dipole moment of $\mu = 0.42 \times 10^{18}$ e.s.u. (or 0.42 Debye). Such an induced moment with the positive end away from the metal would explain the change in contact potential on adsorption. The resulting contribution to the adsorption energy can be evaluated from the following equation²³⁵

$$E_{\alpha} = - \mu^2 / 2 \alpha \quad (149)$$

where α is the polarisability and μ is the dipole moment estimated from contact potentials or the Van der Waals attraction constant. It must be emphasised that unless the adsorbate is an ion, the foregoing analysis shows that the most important contribution to the adsorption energy of a non-polar molecule on a uniform metal surface is due to an induced dipole. This is likely to be true even for molecules possessing small permanent dipoles such as carbon monoxide, or for these possessing quadrupoles such as nitrogen.

(v) Energies of Interaction with Dielectric Surfaces

The interaction energies of adsorbates with dielectric surfaces such as salts and oxides depend on the nature of the approaching molecule. With conducting surfaces the dominating forces we have seen, are due to polarisation of the adsorbate. This is to be contrasted with the situation at dielectric surfaces where Van der Waals interaction and forces arising from interaction with permanent dipoles are predominant. Interactions of non-polar adsorbates with dielectric surfaces arise mainly from Van der Waals forces. The energies due to repulsion and Van der Waals forces have been discussed.

When ions are adsorbed on an ionic lattice, the contribution due to coulombic forces is regarded as relatively small,^{227,236} owing to counter-interaction with ions of the

same sign in the surface. The most important contribution is due to the energy of polarisation of the dielectric given by

$$E_{\beta} = - \frac{z^2 e^2}{4 r_0} \frac{\epsilon - 1}{\epsilon + 2} \quad (150)$$

where ϵ is the static polarisability of the dielectric.

The energy of interaction of polar molecules with ionic crystals is in proportion to their dipole moments according to the equation

$$E_{\mu} = - \mu F \quad (151)$$

where F is the local electrostatic field at the solid interface, and can be estimated from measurements of heats of immersion.²³⁶ This contribution is large for highly polar molecules like water. Polarisation of the adsorbate by the dielectric contributes, however, a small energy even if the molecule is non-polar.

(vi) The Influence of Surface Dipoles and the Dipole Moments of Substrates in Adsorption Processes

Upon adsorption at a metal surface the electrical properties of the adsorbate are generally changed compared with those of the isolated molecules and this effect may depend on extent of coverage of the surface. Among these properties the magnitude of the dipole moment produced on adsorption is of

considerable interest. The surface dipole moment is obtained by measurement of the change in work function $\Delta\chi$, which arises from the modification of the surface double layer and consequent change of the surface potential. The electron work function of a metal varies with the state of the surface because adsorption creates surface dipoles which alter the potential barrier through which the electron passes in escaping from the surface. Changes in the work function have been measured by thermionic emission or photoelectric techniques, but more often by the contact potential method. If the negative end of the dipole produced on adsorption is directed away from the surface (electronegative layer), χ the work function is increased; if towards the surface (electropositive layer), χ is decreased. Mignolet²³¹ has suggested that physically adsorbed films may be characterised by negative values of $\Delta\chi$ and chemisorbed films by positive values.

The effective dipole moment μ can be directly calculated from $\Delta\chi$ provided that the degree of surface coverage θ is known. Values of μ for various systems have been reported. Bosworth and Rideal²³⁷ made measurements of μ using saturated layers of adsorbed gases for which $\theta \rightarrow 1$. $\Delta\chi$ is only directly proportional to θ if μ is independent of θ , but this is not always necessarily the case. For certain layers of metal vapours adsorbed upon tungsten, μ has

been found to decrease markedly as θ increases, owing to mutual depolarisation of dipoles.²³⁸

The magnitude of the dipole moment is in itself an indication of bond type; large μ values suggest ionic or polar bonds and low μ values suggest covalent bonds. Moreover, aligned dipoles repel one another and the repulsion energy increases as θ increases. The effect amounts to a decrease in the heat of adsorption as θ increases. Measurements of heats of adsorption often provide a useful, but not always decisive, approach to the determination of the extent of the interaction. Changes in the electronic work function should be considered in conjunction with the influence of bulk properties of the metal, such as electronic structure, magnetic susceptibility and electrical resistance. Apart from the study of bulk properties of the metal, the best criteria for distinguishing between physical adsorption and chemisorption are afforded by changes in the optical, magnetic or other properties of the adsorbed molecules. In this respect, infra-red spectroscopy has been successfully employed by Eischens²³⁹ and his co-workers for the study of adsorption on metals.

In the case of adsorption from solution, the problem of estimating the exact magnitude of the effective dipole moment of the molecule in the adsorbed state is a practical impossibility. Despite this gloomy realisation, one can

optimistically anticipate a dependence of the adsorption behaviour (e.g. with respect to the variation of heats of adsorption) upon the dipole moment of the additive, e.g. as discussed by Gierst.⁸⁶

(vii) The Role of Hydrogen Bonding and Lone Pair Orbitals in Surface Interactions

Hydrogen bond association has many distinct features, although it is currently regarded as somewhat similar to dipole association. The hydrogen bond is regarded as arising from the purely electrostatic interaction between the relatively unscreened positive charge on the hydrogen nucleus and the electrons in the lone-pair orbitals of the "donor" atom.²⁴⁰ Hydrogen bonding results in certain modifications in the electron distribution of the individual molecules. There is now ample evidence of hydrogen bonding in many two-phase systems^{241, 242} at interfaces.

In electrode processes where adsorption occurs, it will not appear improbable that hydrogen bonding plays an important role, especially in cases where the adsorbate contains an electronegative atom and the solvent is hydroxylic. This point of view was put forward in a recent paper by Gierst⁸⁶ who suggested that N-heterocyclic molecules may orient at the electrode surface with their negative ends towards the solvent. A fuller discussion of this matter was presented in

the light of the author's own experimental findings in Chapter IV of this thesis.

The role of adsorption of the solvent in electrode reactions has not been well characterised, although there is no doubt that the solvent must take part in hydrating or solvating the reacting species and determining the heat of activation of the electrode reaction. Furthermore, the forces with which the solvent is held to the metal surface are at present little understood.²⁴³ A few determinations have been made of the heat of adsorption of water and alcohols at mercury and other metals^{208, 244} and these experiments indicate that the adsorption forces are of a more specific nature than those of physical adsorption, and may involve interactions of unshared electron pairs with the metal and hydrogen bonding between adsorbate molecules in the surface layer.

For the present, it suffices to state that in adsorption from the aqueous liquid phase hydrogen bonding will usually determine the solubility of the additive in the solvent. This can be qualitatively generalised by saying that in adsorption, the metal surface and the solvent attract the additive in an uncompetitive manner. In general, it may be anticipated that the greater the solubility of the adsorbate the less will the substance tend to be adsorbed at the metal surface, although this is not always the case as has been

shown above in the section on Experimental Results.

(viii) The Effect of Unshared Lone Pair Electrons
in Adsorption

Coordinate links may sometimes be formed with the adsorbent in the chemisorption of molecules containing atoms of groups V and VI of the periodic table. The linkage takes place by the "donation" of electrons from the adsorbate to the adsorbent. Maxted and his co-workers²⁴⁵ have studied the poisoning of transition metal catalysts and provided evidence (e.g. the loss of paramagnetic susceptibility of palladium upon adsorption of dimethyl sulphide) for the existence of such bonds.

Poisoning effects by non-metals on a variety of catalytic reactions in solution were found to be largely confined to those compounds of elements of groups V and VI that possess lone electron pairs. The following table (Table XIV) illustrates some examples of the influence of electronic configuration on toxicity:

TABLE XIV

Element	Toxic Compounds	Non-toxic Compounds [*]
N	$ \begin{array}{c} \text{H} \\ \\ \text{C} \\ / \quad \backslash \\ \text{HC} \quad \text{CH} \\ \quad \\ \text{HC} \quad \text{CH} \\ \backslash \quad / \\ \text{N} \\ \\ \text{NH}_3 \end{array} $	$ \left[\begin{array}{c} \text{H} \\ \\ \text{C} \\ / \quad \backslash \\ \text{HC} \quad \text{CH} \\ \quad \\ \text{HC} \quad \text{CH} \\ \backslash \quad / \\ \text{N} \\ \\ \text{NH}_4^+ \end{array} \right]^+ $
P	$ \begin{array}{c} \text{H} \\ \\ \text{H} - \text{P} - \text{H} \\ \\ \text{..} \end{array} $	$ \left[\begin{array}{c} \text{O} \\ \\ \text{O} - \text{P} = \text{O} \\ \\ \text{O} \end{array} \right]^{3-} $
As	$ \begin{array}{c} \text{H} \\ \\ \text{H} - \text{As} - \text{H} \\ \\ \text{..} \end{array} $	$ \left[\begin{array}{c} \text{O} \\ \\ \text{O} - \text{As} = \text{O} \\ \\ \text{O} \end{array} \right]^{3-} $
S	$ \left[\begin{array}{c} \text{O} \\ \\ \text{O} - \text{S} - \text{O} \\ \\ \text{..} \end{array} \right]^{2-} $	$ \left[\begin{array}{c} \text{O} \\ \\ \text{O} - \text{S} = \text{O} \\ \\ \text{O} \end{array} \right]^{2-} $
	$ \text{R} - \text{CH}_2 - \begin{array}{c} \text{..} \\ \text{S} \\ \text{..} \end{array} - \text{CH}_2\text{R} $	$ \text{RCH}_2 - \begin{array}{c} \text{O} \\ \\ \text{S} \\ \\ \text{O} \end{array} - \text{CH}_2\text{R} $
	$ \begin{array}{c} \text{..} \\ \\ \text{HC} \quad \text{CH} \\ \quad \\ \text{HC} \quad \text{CH} \end{array} $	$ \begin{array}{c} \text{O} \quad \text{O} \\ \backslash \quad / \\ \text{S} \\ / \quad \backslash \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \quad \\ \text{H}_2\text{C} \quad \text{CH}_2 \end{array} $

* These structures are written with conventional coordinate covalent linkages. In some cases this representation may be regarded as archaic ²⁴⁶ but is adequate for illustrating the differences of structures discussed here.

Catalyst poisons are normally effective through being very strongly adsorbed and covering the "active" part of the surface. Since poisoning activity is mostly limited to compounds capable of coordination it appears likely that the poisons are adsorbed in this way, possibly with donation to a metal d-band "hole" (vide infra). The adsorption of ammonia (and possibly phosphine and arsine) appears to be an exception. Thus, evidence is provided by the work of Wahba and Kemball²⁴⁷ in their studies of ammonia chemisorbed on tungsten, iron and nickel films, that adsorption involves dissociation and the formation of covalent bonds.

The coordinate linkages discussed by Maxted may be illustrated in the following types of chemisorption where the full arrow is used to signify the coordinate linkage.

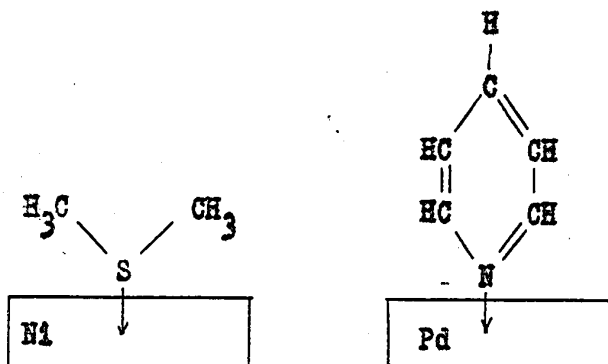
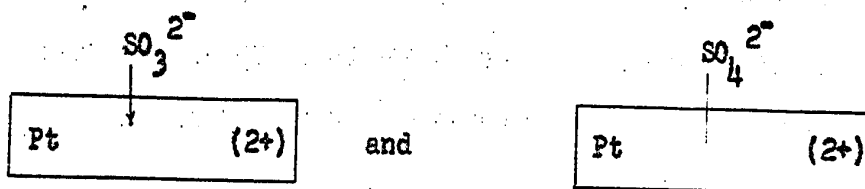


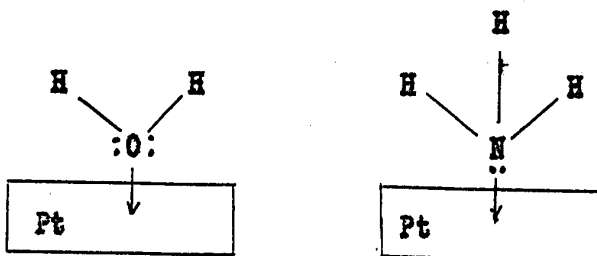
Table XIV shows that donor elements do not exhibit catalytically toxic properties when they are in their highest state of valency, i.e. when there is no lone pair of electrons available. The same holds for ions of these elements; the sulphite ion

acts as a poison, whereas the sulphate ion does not:



The former is bound by a coordinate link, aided by the force of interaction with the image (2+) of the ionic charge; the latter force is, however, rather weak because of the relatively large distances of the negative excess charges from the metal. In the absence of other chemical factors such as surface salt formation, the sulphate ion is held only by this image force. In both cases there are the Van der Waals forces in addition but these will be weak.

Suhrmann^{2,8} has explained the strong increase of the normal photoelectric effect at metals caused by the adsorption of water and ammonia by suggesting the formation of similar coordinate links with the metal in the chemisorption of these molecules. Dipoles are formed which are oriented with their positive poles away from the surface, thereby decreasing the electronic work function and consequently lowering the normal photoelectric threshold.



Hackerman and Makrides²¹⁶ suggested in their study of the action of polar organic corrosion inhibitors on the rates of dissolution of metals in acids that chemisorption of inhibitors occurs through coordinate bond formation with the surface atoms of the metals. The inhibitor is regarded as acting as the donor and the metal as the acceptor. They showed that polar organic compounds containing elements of groups V and VI are effective as inhibitors. Some particularly effective functional groups are $-CH_3$, $-CNS$, $-CNO$, $=CO$ and $-CHO$, and compounds which contain them are "electron rich", and can act as electron donors. Hackerman and Makrides suggested that a satisfactory explanation of the inhibitory effectiveness of these compounds can be given along lines similar to those stated in Maxted's work. The two cases are comparable in that adsorption of the additive is the important factor in both examples.

Further evidence for the role of lone pair electrons has been provided by Hackerman and Cook^{249, 250} in their study of adsorption of inhibitors from benzene solutions onto steel powder. It was also pointed out that not more than one electron pair per inhibitor molecule will be donated to the metal surface, although the acceptor might have available orbitals for more. Chemisorption can also occur when the metal acts as donor and the adsorbate as acceptor.²⁵¹

Chemisorption could cause inhibition either by decreasing the dissolution tendency of the metal or by increasing

the activation overpotential for hydrogen discharge, i.e. by poisoning the cathodic reaction. The corroding metal presents, of course, an almost equipotential surface to the solution; the (aqueous) corrosion process then occurs by the simultaneous passage of anodic and cathodic partial currents at a mixed potential determined by the polarisation parameters for the partial reactions.

Hackerman and Makrides²¹⁶ showed that the relative order of effectiveness of aliphatic amines as inhibitors for corrosion of iron was:

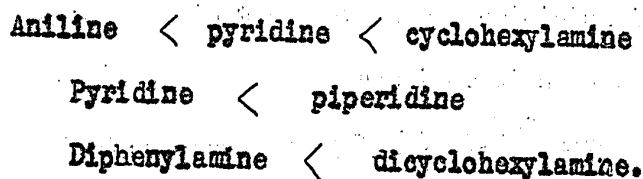
$\text{NH}_3 < \text{RNH}_2 < \text{R}_3\text{N} < \text{R}_2\text{NH}$ where R is a methyl group, and also $\text{NH}_3 < \text{RNH}_2 < \text{R}_2\text{NH} < \text{R}_3\text{N}$ where R may be ethyl, propyl, butyl or amyl groups.

In all these cases cited, the strength of the iron-amine bond was suggested as being a function of both electron density on the N atom and the availability of these electrons for coordinate bond formation with the metal. It was shown that the introduction of a fourth alkyl group (to give the quaternary ion) caused a sharp drop in inhibitory power. On the basis of this theory such a decrease in inhibitory power is understandable. However, Conway, Barradas and Zadwidzki¹⁸⁷ (see also Chapter V) showed by direct spectrophotometric measurements of the adsorption of the quaternary N-methyl acridinium ion, that the ion was as strongly adsorbed as the

neutral molecule but in this case the N atom still has a π -orbital available for adsorption to the metal and in this respect the N atom in the quaternary acridinium ion is not in an electronically analogous configuration to that in aliphatic quaternary salts. Chappell et al.¹⁶³ have also demonstrated inhibition by the quaternary salt quinoline ethiodide upon the corrosion of iron but the effect is less strong than with aliphatic non-quaternised compounds. It is apparent, therefore, that some factors in addition to the availability of a lone pair of electrons may be involved in determining the strength of adsorption of N-containing additives. In a series of similar S, N and O compounds, the trend of adsorbability is $\text{RSH} > \text{RNH}_2 > \text{ROH}$; this is also the reverse order of electronegativity of the three atoms, i.e. the order of decreasing electron donative power and electronic polarisability.

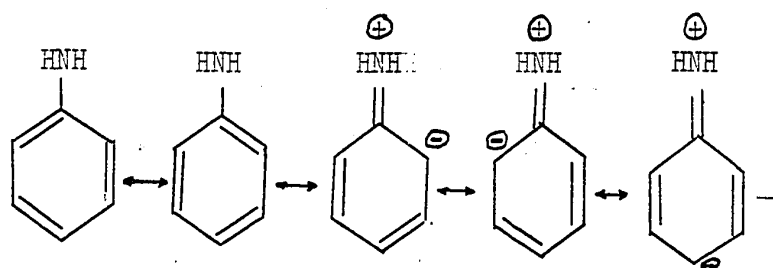
Hackerman and Makrides also established some interesting relationships between inhibitory power and molecular structure of aromatic and heterocyclic organic compounds. When the inhibiting functional group was attached to an aromatic nucleus, the corrosion inhibiting power was diminished in comparison with that of alicyclic or aliphatic analogues. Aliphatic amines were found to be better inhibitors than aromatic amines. Heterocyclic amines, while still better than aromatic amines, are less effective than the corresponding

saturated compounds. These relations are exemplified by the following scheme:



Comparative determinations of the electrochemical free energies of adsorption of some of these compounds are reported in Chapter IV of this thesis.

The introduction of alkyl groups on the benzene ring of aniline leads to better inhibition because of both decreased solubility and increased electron density on the N atom. The same is true when hydrogen atoms on N are replaced by alkyl groups. This may be interpreted in terms of the tendency of the aromatic ring to withdraw the unshared pair of electrons away from the donative N atom. Conversely, when electron repelling groups such as alkyl groups are introduced into the aromatic ring some inhibiting effectiveness is regained.²¹⁶ Qualitatively, this can be explained from the following example; aniline can be represented by five canonical forms which contribute to the overall structure



Substitution of electron-donating methyl groups in the ring decreases the contribution of the last three structures and tends to lead to increased chemisorption presumably because of the resulting greater electron density at the N atom. From these structures it seems reasonable that, other things being equal, substitution in the ortho or para positions should be more effective than substitution in the meta position.

(ix) Effect of Unsaturation and π -orbital Interaction

Studies of chemisorption of ethylenic compounds on metal catalysts have been extensively reported in the literature. The larger degree of interaction of unsaturated compounds with surfaces is attributed to enhanced chemisorption brought about by the double bond, which can contribute a second point of attachment of the adsorbate. Two point contact for the adsorption of ethylene on nickel has been reported by Twigg and Rideal²⁵² but this probably involves dissociation. The chemisorption of acetylene on nickel by two point contact has also been discussed by Herington.²⁵³

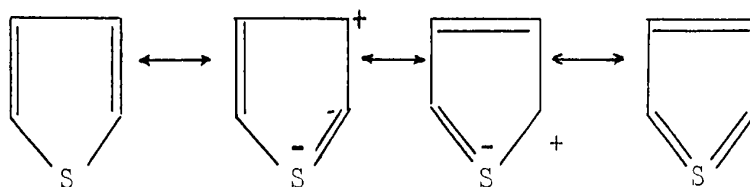
A change in the work function of metal surfaces upon adsorption of foreign molecules is to be expected only if an electron shift occurs to or from the metal surface. If the electrons of adsorbed molecules become part of the metal "electron gas", or if the metal electrons become involved in the electronic shell of the molecule, not only a change of work

function but a change in the electrical resistance of the metal will also be observed. The change of resistance will usually become of measurable magnitude when the adsorbing metal is not thicker than approximately a hundred to a thousand times the thickness of the layer undergoing electronic interaction with the adsorbate. For such systems, measurements of electrical resistance of transparent metallic layers can give valuable data on the type of electronic interaction involved.

Suhrmann and Sachtler²⁵⁴ showed that the work function of platinum foil was lowered by the adsorption of benzene. They concluded that the π -electrons were displaced to the metal surface by adsorption. Suhrmann and Schulz^{255,256} demonstrated that the electrical resistance of nickel films drops when benzene or naphthalene is adsorbed. Again the conclusion is that π -electrons of the ring actually became transferred to the metal and result in a lowering of the resistance. A similar behaviour of the resistance of transparent nickel films was observed in the case of adsorption of triphenylmethane.

Smith and Meriwether²⁵⁷ found that the catalytic hydrogenation of benzene on platinum was of zero order with respect to benzene and had an activation energy of 7.4 kcal mole⁻¹; they suggested that this low value, compared with the resonance stabilisation energy of benzene (36 kcal mole⁻¹)

indicated that benzene was chemisorbed in such a way that resonance was destroyed; however, the logicity of their argument is doubtful. Maxted and Joseph²⁵⁶ have discussed the anomalous calorimetric heats of adsorption of thiophene in relation to that of diethyl sulphide on platinum surfaces. The canonical forms of thiophene are as follows:



The values of the heats of adsorption suggest that thiophene, like benzene, loses its resonance energy on adsorption. Maxted and Joseph observed that the initial heat of adsorption of diethyl sulphide was, surprisingly enough, considerably larger than that of its ring analogue, thiophene. The difference agrees with the known resonance energy of thiophene. The evidence is unmistakable that the stabilising resonance energy must be "paid for" in the adsorption of thiophene. Presumably, as in the case of benzene, the π -electrons of the ring add to the metal and the energy ($+ 35 \text{ kcal mole}^{-1}$) associated with destruction of the resonance upon adsorption is then lost so that the numerical heat of adsorption is anomalously

low.

Further evidence of interaction due to π -electrons has been given by Selwood,²⁵⁹ who measured the loss in magnetic susceptibility of supported nickel upon the adsorption of hydrogen, benzene and cyclohexane. The initial rate of fall of heat of adsorption with surface coverage for these three adsorbates is very approximately in the ratio of 2:6:8. This relationship is expected if the hydrogen molecule splits to become chemisorbed as atoms and if one hydrogen splits off each of the four carbon atoms in cyclohexane which contact the surface in the "boat" configuration; no hydrogen splits off from the planar benzene ring, in which case six contacts are made.

The role of π -electron interaction with the mercury surface and at solid electrodes have been examined in some detail in this thesis. It suffices here to recapitulate briefly some of the earlier work done on this topic. Gerowicz^{182,183} compared the electrocapillary behaviour of pairs of aromatic and corresponding hydroaromatic hydrocarbons such as benzene-cyclohexane and naphthalene-decalin. From these experiments Gerowicz proposed that on the positive branch of the electrocapillary curve the principal force of adsorption of molecules of aromatic compounds arises from interaction between π -electrons of the aromatic nucleus and the positive charges on the mercury surface. Gerowicz and Rybal'chanko¹⁸⁴ extended similar electro-

capillary studies to unsaturated alicyclic and aliphatic compounds. They showed that the degree of adsorbability parallels the amount of unsaturation present in corresponding compounds. It was also shown that the position of the double bonds in the compounds had a very significant effect on the adsorption at mercury. A comparison was made between 1,5-hexadiene and 2,4-hexadiene and the experimental results clearly indicated that the compound with the conjugated system of double bonds exhibited the greater adsorbability. It may be stressed that the above-mentioned work was carried out in non-aqueous solvents. During the course of the work reported in this thesis, Bockris and Blomgren³¹ published some results of electrocapillary investigations of several organic amines in 0.1 N aqueous hydrochloric acid solutions. They reported that the principal effective force of adsorption operating on the positive (or anodic) branch of the electrocapillary curve is due to π -electron interaction with the mercury surface but the interpretation of their results was directed essentially towards explanation of the mechanism of corrosion inhibition.

It is relevant to mention here the quantum mechanical calculations of π -electron energy differences ($\Delta\pi$) between several quinones and corresponding hydroquinones reported by Basu.^{260,261} His results may be summarised as follows

$$\Delta\pi = 2 \times + 0.56 h^2/8 m l^2 \quad (152)$$

where α is the π -electron energy in a carbonyl group and the secondary term is the π -electron energy of two ethylenic double bonds calculated by the free electron approximation method (cf. Kauzmann²⁶²), h is Planck's constant, m the electron mass and l the length of a C-C double bond. Small values of $\Delta\pi$ correspond to a greater ease with which quinones will form from the parent hydroquinone. $\Delta\pi$'s were also calculated for phenols. A correlation was found between the π -electron energy-difference and actual oxidation potentials of a number of phenols. An unsuccessful attempt was made to correlate the polarographic half-wave potentials of a number of open-chain aldehydes with $\Delta\pi$ between the oxidised and reduced forms; the process was assumed to be a one electron plus one proton addition at the dropping mercury cathode.

C. NATURE OF ADSORBENT SURFACES AND INTERNAL STRUCTURES

(1) General Remarks

In recent years a concerted effort has been made to connect chemisorption behaviour with the properties of solid catalysts which will permit an a priori prediction of their specific catalytic activity. Two such important properties have emerged: the geometrical and electronic factors. It is to be noted that the discussion which follows will be necessarily brief since several excellent reviews on these subjects have

appeared in the literature.^{238,263-266}

(ii) Geometrical Factors

Since the classical work of Langmuir²⁶⁷ and Taylor,²⁶⁸ crystal structures and molecular bond lengths have become more precisely known, and it is natural that correlations should be sought between the geometry of a solid surface and its adsorptive power or catalytic activity. Considerable theoretical and experimental support for the operation of factors concerned with surface geometry has been published.^{282,253,269,275} For example, during the period 1934-1948 Beeck²⁷²⁻²⁷⁵ and his co-workers carried out their classical experiments on the study of the catalytic hydrogenation of ethylene over metallic films. They reached the conclusion that the activity of these metal films for this reaction was apparently related to certain inter-atomic spacings in the metal. They plotted the activity against the lattice spacings of a series of metals and their results indicate that the spacing of atoms in rhodium was optimum for the ethylene hydrogenation.

(iii) Electronic Factors

Contemporaneously with the introduction of the geometric factor, a second and more general factor appeared in the literature of chemisorption. This is the so-called "electronic factor", which is implicit in certain papers

published as early as the 1920's.^{276,277} Inasmuch as the edge of the unit cell of metal catalysts with cubic lattices may be the gauge of the geometric factor, the magnetic properties of the metal are a measure of the electronic factor. Furthermore, the high energies of binding observed in chemisorption imply that the forces involved are the electronic ones familiar in ordinary chemical bond formation and thus in any theoretical treatment of chemisorption, considerations both of electron transfer between the solid and the adsorbate and of electron sharing become necessary. Since electrons must be provided or accepted by the solid adsorbent, it is clear that the electronic structure of the solid must play a principal role.

Several workers²⁷⁸⁻²⁸² have attempted quantum mechanical treatments of the electronic factors in chemisorption. While this theoretical approach is important, it has not progressed sufficiently far to be able to yield conclusions capable of examination by experimental measurements on real systems. A more fruitful approach to the theory of chemisorption has been the application of the electron theory of metals at a much less formal level, with the immediate aim of interpreting existing data qualitatively. This semi-empirical approach provides a firmer footing for future endeavour and particular mention should be made of the work of Dowden.²⁸³⁻²⁸⁵

Applications to electrochemical reactions have been made by Conway and Bockris³⁰⁴ and by Schuldiner et al.³⁰⁷

Hydrogenation catalysts are usually transition elements. The atoms of these elements possess partly empty d-shells and the electronic properties of the bulk metal may be treated in terms of two complementary theories: the one based on the band theory developed by Mott and Jones²⁸⁶ and the other on the valence bond theory of Pauling.²⁸⁷ Pauling showed that the lattice spacings of transition metals are closely related to their "d-character" and the interesting possibility arises that in some cases the apparent existence of a geometric factor may more fundamentally be related to the electronic structure of the metals.

Boudart²⁸⁸ using Beek's original data for the correlation between crystal parameters and catalytic activity in ethylene hydrogenation, found that the logarithm of activity was a steadily increasing function of percent d-character. The term "d-character" is regarded as a measure of the degree of participation of d-electrons in the dsp hybrid bonding between metal atoms. Increasing participation of d-orbitals means that more d-electrons are used for the mutual cohesion of the metal atoms in the metallic crystal lattice. This also means that fewer d-electrons are available for chemisorption. The hypothesis that a high d-character favours covalent

chemisorption is borne out by direct studies of adsorption. The best indications of this are for those reactions catalysed by binary alloys in a certain range of composition where the d-band is completely filled from a certain composition onward (for example the work of Couper and Eley,²⁸⁹ Dowden and Reynolds,²⁹⁰ Rienacker and Vermum²⁹¹ and Maxted, Dilke and Eley²⁹²).

However, Sheridan and Reid,²⁹³ working on acetylenic hydrogenation, demonstrated that no clear relationship existed in this case between percent d-character and catalytic activity. They found instead a parallelism between catalytic activity and magnetic susceptibility, which arises intrinsically from the presence of d-holes in the metal. This points therefore to the more currently accepted view that adsorptive properties and catalytic activity is essentially dependent on the number of d-holes or unpaired d-atomic orbitals and not necessarily on percent d-character. For hydrogenation reactions there is some fortuitous correlation between catalytic activity and d-character in the transition elements but this is not general. It may be remarked that the variation of percent d-character in those transition elements discussed by Beeck and Boudart was quite small so that it is not perhaps surprising therefore that apparently linear relationships between activity and d-character were obtained. Catalytic activity

and heats of adsorption will depend more fundamentally on the number of unpaired d-atomic orbitals (Pauling) or d-holes (Mott and Jones). It may also be seen from the following table that there is no simple relation (e.g. a reciprocal one) between the number of unpaired d-atomic orbitals in the metal and the percent d-character.

TABLE V

Elements	Fe	Co	Ni	Cu
% d-character	39.7	39.5	40.0	36.0
Unpaired d-atomic orbitals	2.2	1.7	0.6	0

This table has been taken from McD. Baker and Jenkins, ref. (265).

(iv) Overpotential and Hume-Rothery Alloys

Studies of hydrogen overpotential also provide some evidence for the [^]role of electronic structure in (electro-) catalysis by metals. Thus Himmler²⁹⁴ found that the overpotential at a copper electrode is increased by alloying with higher-valent metals. As the electron to atom ratio in the α phase is increased, thereby filling the Brillouin zone, the overpotential is found to be increased.

Before proceeding further, a short digression on a few fundamental concepts will be of aid in the ensuing discussion. The energy bands within which an electron may be transferred from one energy state to another without crossing one of the discontinuities, i.e. without involving any large increments of energy, are known as Brillouin Zones. The progressive substitution of one type of metal atom by another type having a different valency changes the ratio of valence electrons to metal atoms in the crystals. This ratio has been termed the Electron Concentration (E.C.). The Fermi level (the envelope of the highest occupied quantum states) of the "solute" metal will either be raised or lowered depending on whether the solute metal has a higher or lower valency.

Hume Rothery^{295, 296} pointed out that in some alloys the structure of the inter-metallic phases are determined by the E.C. The series of changes $\left[\alpha \text{ (F.C.C.)} \rightarrow \beta \text{ (B.C.C.)} \rightarrow \gamma \text{ (complex structure)} \rightarrow \epsilon \text{ (C.P.H.) phase} \right]$ which occur as the composition of an alloy is varied continuously, take place at electron to atom ratios of $3/2$, $21/13$ and $7/4$, respectively. The interpretation of these changes in terms of the Brillouin Zone theory has been made by Jones,²⁹⁷ and he obtained theoretical values which are in excellent agreement.

Metals, for example silver, are able to dissolve other metals to form stable Hume-Rothery phases. Electrons

from the solute metal fill up the vacant electron levels in the Brillouin zone until a solubility limit is reached. Thus, as the concentration of the solute metal is increased, the number of empty electron levels available is diminished. If electron sharing or electron transfer are important in chemisorption, such a change in the electronic structure of the alloy as the zone becomes more complete might well be expected to affect the catalyst activity. The possibility of using these alloys as catalysts of controlled E.C. has been exploited by Schwab and his co-workers,²⁹⁸⁻³⁰⁰ whose exhaustive studies of the decomposition of formic acid vapour over alloy catalysts represent a major contribution in this field.

Using silver or gold as solid solvents and adding the multivalent metals of Groups II to V, the electron concentration can be increased up to 1.33 in the fifth period (Cd, In, Sn, Sb), and to an electron concentration of 1.1 in the sixth period (Hg, Pb, Bi). Although the metals of groups II to V, with atomic radii greater than that of silver ($r = 1.44 \text{ \AA}$), increase the energy of activation (E_A) of the catalysed dehydrogenation of formic acid, the same was found for copper ($r = 1.28 \text{ \AA}$), zinc ($r = 1.37 \text{ \AA}$) and gallium ($r = 1.39 \text{ \AA}$). There is, however, a straightforward correlation between E_A and E.C.; E_A increases with the square of E.C. within the α phase. With heterogeneous alloys of the Hume-Rothery type, other intermetallic phases are formed and

Schwab showed that E_A reached a maximum for each phase.

The catalytic activity of both homogeneous and heterogeneous alloys ^{is} ~~are~~ dependent on the degree of completion of the Brillouin zones. Within a phase domain, addition of a solute metal has the effect of raising the Fermi level, which causes a corresponding rise in the energy of activation. The change from a saturated phase to an unsaturated phase on the Mott and Jones theory is accompanied by a lowering of the Fermi surface, and this produces a lowering of the energy of activation. One infers therefore that the filling up of the Brillouin zone corresponds to the completion of holes in the d-band.

Returning now to the interesting observations made by Himmeler on changes of overpotential, it may be further noted that ~~trivalent~~ ^{such} metals as aluminium and indium had twice the effect of the divalent metal zinc in increasing the overpotential at the copper alloy electrode. Bockris and Pentland³⁰¹ and Bockris and Potter³⁰² have suggested that the slow step in the evolution of hydrogen at copper and nickel electrodes is the production of chemisorbed hydrogen atoms. Thus it is plausible to associate Himmeler's effect with hydrogen chemisorption. The chemisorption of hydrogen at copper, at best a difficult process,³⁰³ will be rendered more difficult as the states in the Brillouin zones are filled further. Bockris³⁰¹ has pointed

that
out/the hydrogen overpotential of a metal is higher, the lower
the work function of the metal. This finds a direct explanation
on the present view, since according to Dowden the promotion
of an electron to the Fermi level, in the formation of a covalent
bond M-H, is an easier process if the work function is large.
Conway and Bockris³⁰⁴ have examined the dependence of hydrogen
overpotential upon work function and heats of chemisorption of
hydrogen at metals. They conclude that the dependence of
exchange currents upon the work function arises indirectly on
account of the primary dependence of electrochemical rates of
hydrogen evolution upon the heat of adsorption of hydrogen on
the one hand, and the dependence of these heats of adsorption
upon work function on the other. Increasing work function is
paralleled by a decrease of heat of adsorption of hydrogen in
a series of transition metals and the observed dependence of
hydrogen overpotential upon work function is then best
interpreted in terms of the decreasing heat of activation for
an electrochemical hydrogen atom desorption step as the
work function increases. This assignment of mechanism is
consistent with the observed magnitudes of H/D isotope
effects.^{305,306}

The kinetics of hydrogen evolution at gold, β phase
palladium-hydrogen and gold-palladium alloys of Au/Pd ratios
of 0.24, 0.43, 0.88 and 2.70 were determined by Schuldiner

and Hoare.³⁰⁷ The rate controlling step for the hydrogen producing reaction on the Pd/H alloy and the Au/Pd alloys up to a Au to Pd ratios of 0.6 was electrochemical hydrogen desorption; beyond this ratio and for pure gold, the rate-controlling step was the combination of adsorbed hydrogen atoms. The effect of successive additions of gold in the alloy on the decrease in catalytic activity of palladium was large up to the 0.5 Au/Pd atomic ratio, but at higher ratios the successive addition of gold produced a much smaller decrease in catalytic activity. Similar effects with Cu-Ni alloys have been found by Conway, Beatty and de Maine.³⁰⁸

Lastly, Burgers and Brabers³⁰⁹ have shown that the rate of cathodic reduction of ferricyanide ions at alloy electrodes is related to the degree of completion of the Brillouin zone in Hume-Rothery alloys, and to the number of d-band holes for transition metals.

It must be cautioned that an exact correlation of the catalytic activity of metals with their solid state properties cannot be made so adequately as the corresponding relationship between the chemisorption of simple molecules and the metallic properties. This circumstance hinges, in part, on the deficiencies of the present state of theoretical development in the field of catalysis, but also on the complexity of the phenomena, on the fact that the mechanisms

of the reactions or adsorption processes concerned are not in many cases unequivocally known, and on the paucity of data. Nevertheless, useful information continues to be gained, although to a large measure still leads only to the derivation of qualitative relationships.

D. CONCLUDING REMARKS

The problems associated with studies of chemisorption and physical adsorption have been outlined in various parts of this thesis. Some of these difficulties are further complicated in studies of "Electrochemical Adsorption" by the presence of solvent molecules in the solution phase and the variable field and electronic state of the surface at various electrode potentials. In spite of these problems, the barriers to further progress are not insuperable.

In conclusion, an abridged summary of the principal factors which determine the adsorption of additives and solvent at electrodes is given below:

1. Van der Waals Forces
2. Electrostatic Image Potentials
3. Nature of the Chemical Bond between Adsorbate and Adsorbent
4. [^]Role of Hydrogen Bonding
5. Polarisability and Orientation of Surface Dipoles
6. π -Electron Interaction

7. Interaction of Lone Pair Orbitals
8. Resonance Effects in the Adsorbate Species
9. Structure and Geometry of Adsorbates
10. Effect of Dipole Moments
11. Effect of Electron Work Functions
12. Solvation Effects
13. Purity and State of Adsorbent Surface
14. Nature of adsorbent Structure: Electronic and Geometric Factors, in particular the d-hole vacancies in transition metals and electron concentration in alloys
15. Impressed Field-dipole Interactions in the double layer
16. Impressed field-charge interactions in the double layer
17. Competitive effects between solute and solvent for the electrode surface and for the region of high field intensity near polarised electrodes
18. Classical "surface activity" effects connected with solubility and solvation of the additives (independent of the metallic phase and found also e.g. at the air-water interface).

CLAIMS TO ORIGINAL RESEARCH

I. NEW EXPERIMENTAL RESULTS AND THEORETICAL INTERPRETATIONS

1. Electrochemical isotherms for several un-ionised organic bases, their conjugate protonated and their N-methyl quaternary salts have been determined at mercury.
2. The thermodynamics of the isotherms have been examined and, in particular, a direct comparison between the standard electrochemical free energies of adsorption of several un-ionised bases and their conjugate ions have been made for the first time.
3. Interaction effects in the adsorbate layer have been deduced from the thermodynamic data for the organic bases both in the ionic and neutral forms.
4. A theoretical treatment for such interaction effects between the neutral adsorbate molecules has been developed and shown to be semi-quantitatively applicable to the experimental results.
5. Important orientation effects in the adsorbate layer have been correlated with molecular structure and field in the electrical double layer.
6. The theoretical treatment for interaction effects with ionic adsorbates has been improved and also shown to be applicable to the appropriate experimental results.

7. New information on the structure of the double layer in the presence of organic ions and molecules has been obtained by a detailed evaluation of the ionic components of charge as a function of electrode potential, adsorbate concentration and acid concentration.
8. The Esin and Markov coefficients (i.e. the factors determining the slope of the relation between the potential at the e.c.m. and the chemical potentials of the adsorbate in solution) have been evaluated experimentally for the organic ions and shown to be in agreement with corresponding values deduced thermodynamically.
9. An analogous treatment to that mentioned in (8) has been given for the first time for neutral molecules, and the theoretical and experimental slopes compared.
10. The role of π -orbital effects in determining the electrochemical free energies of adsorption of the various additives has been critically examined and discussed quantitatively in several cases.
11. From comparative data on components of charge and on electrochemical free energies of adsorption for structurally related N-protonated and N-alkylated heterocyclic ions, it has been concluded that in these cases the principal species adsorbed in acid solutions of the bases are the protonated ions.

12. Isotherms have been obtained for several heterocyclic bases at copper, nickel and silver, and interpreted thermodynamically.

II. NEW EXPERIMENTAL TECHNIQUES

1. Minor improvements in the technique of electrocapillary measurements and in the design and operation of the Lippmann Electrometer have been reported.
2. A new technique for determination of the adsorption of organic additives under equilibrium conditions at solid electrodes has been developed and utilises a spectro-photometric analytical procedure.

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